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SECONDARY ARSINES.

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The first secondary arsine, dimethylarsine or cacodyl hydride, was prepared by Palmer.[1] He reduced cacodyl chloride by means of platinized zinc and hydrochloric acid, in alcoholic solution, the reaction being:

$$(CH_3)_2AsCl + 2H = (CH_3)_2AsH + HCl.$$

Since the preparation of cacodyl chloride from cacodyl oxide, by treatment with mercuric chloride and hydrochloric acid,[2] is attended with considerable inconvenience, an easier application of the principle of the general reducibility of alkylated arsenic compounds[3] was attempted, *viz.*, the direct reduction of the crude "arsenical liquors of Cadet." It was found that the following reactions took place smoothly and quantitatively, though the yields were, of course, limited by the possibility of condensation of arsine vapors from the excess of hydrogen evolved:

[1] Ber. d. chem. Ges., 27, 1378.
[2] Ann. Chem. (Liebig), 107, 262.
[3] THIS JOURNAL, 33, 105.

$$[(CH_3)_2As]_2 + 2H = 2(CH_3)_2AsH,$$
$$[(CH_3)_2As]_2O + 4H = 2(CH_3)_2AsH + H_2O.$$

Thus a needless operation, that of transforming crude cacodyl into cacodyl chloride, is eliminated, and dimethylarsine can now be prepared with greater ease than any primary or tertiary arsine or any other secondary arsine.

Crude Cacodyl.

This substance, the first known organic compound containing arsenic, was observed by Cadet in 1760, when he distilled a mixture of arsenic trioxide and potassium acetate and obtained a very offensive, heavy, fuming, yellow oil which has since been known as "Cadet's fuming arsenical liquid." In his researches on the cacodyl series, Bunsen[1] found that this substance is a mixture of cacodyl and cacodylic oxide, the latter being present in by far the larger proportion, the former causing the fuming and spontaneous inflammability[2]. No improvement in the yield of this substance has been made since the time of Bunsen, though in 1858 Baeyer[3] made experiments with this end in view. By proceeding in the manner described below, we have been able to obtain yields somewhat larger than 30 per cent; these yields, however, include cacodyl, cacodylic oxide and cacodylic acid, all of which are usable for the preparation of dimethylarsine.

An intimate mixture of 250 grams of arsenic trioxide and 250 grams of anhydrous potassium acetate is heated in a short-necked, hard glass flask, of about 500 cc. capacity. The flask is placed in a hemispherical iron cup containing a little sand and is then connected, through a Liebig condenser, with a filter flask used as a receiver. It is advisable to surround the receiver with ice water and to connect its exit-tube with wash bottles containing mercuric oxide, so that all of the crude cacodyl may be condensed or oxidized to cacodylic acid and thus be completely retained. During the course of 8–10 hours, or until the evolution of carbon dioxide ceases and no

[1] Ann. Chem. (Liebig), 37, 6.
[2] *Ibid.*, 37, 6.
[3] *Ibid.*, 107, 261.

more distillate is collected, the temperature of the flask containing the potassium acetate and arsenic trioxide is gradually raised and continued at a dull red heat. The distillate is found to have collected and separated into 3 distinct layers; the lowest layer, small in quantity, is composed of reduced arsenic or polymerized products (*vide* p. 10); the middle layer, a dark yellow oil, consists of cacodyl and cacodylic oxide; and the upper layer, largest in volume, contains a solution of cacodylic oxide in acetone, acetic acid and water. The second layer is conveniently separated and used directly for the preparation of dimethylarsine; the upper layer is treated with mercuric oxide and, together with the contents of the wash bottles, is filtered and evaporated to a small volume, when it can be reduced to dimethylarsine. By the most careful and intense heating the largest yield of cacodylic oxide was 25 per cent.; the amount of cacodylic acid obtained increased the yield so that it exceeded 30 per cent.

Reduction of Cacodylic Oxide to Dimethylarsine.

The reduction of cacodylic oxide to dimethylarsine is conducted in a manner similar to that employed in the preparation of methylarsine. Amalgamated zinc dust (250 grams), cacodylic oxide (50 grams) and alcohol (200 cc.) were placed in a 1-liter, round-bottomed flask, to which were connected in order, a water wash bottle, a U-tube filled with soda-lime, the condenser used for methylarsine,[1] a sulphuric acid wash bottle and a nitric acid wash bottle. The connections were made of glass and cork throughout, because the arsines attack rubber with great avidity. After surrounding the condensing bulbs with a freezing mixture of salt and ice, concentrated hydrochloric acid is slowly admitted to the reduction flask, through a dropping funnel. After a few minutes a bright yellow substance forms and indicates a partial reduction; this color disappears as the reduction proceeds. Some little time intervenes between the beginning of the evolution of the hydrogen and the passage of the dimethylarsine. The beginning of the evolution of the arsine is detected when the passage of the evolved

[1] Ber. d. chem. Ges., 34, 3594.

gases is faster through the wash bottle next to the reduction flask than it is through the sulphuric acid bottle beyond the condensing apparatus. This period of time intervening between the beginning of the reduction and the evolution of the arsine is undoubtedly consumed in the reduction of the cacodylic oxide to cacodyl—the intermediate product of the reduction :

$$[(CH_3)_2As]_2O + 2H = (CH_3)_2As.As(CH_3)_2 + H_2O.$$

This period of time is longer when cacodylic acid is used instead of crude cacodyl; the former requires 6 atoms of hydrogen, the latter requires 2–4 atoms of hydrogen, depending upon the relative proportions of the cacodyl and cacodylic oxide present.

When the apparatus contains air a red body is always formed on the inner surfaces of the apparatus. This substance is similar in composition to the red compounds formed in the Wurtz condensations to be mentioned further on and discussed under oxidations (*vide* p. 10).

As the reduction proceeds liquid arsine may be drawn off from the condenser bulbs and sealed in bulbs or constricted test tubes. In this manner 50 grams of cacodyl may be reduced in the course of 2 hours. Occasional shaking of the reduction flask is necessary because the cacodyl coats the zinc and prevents the action of the hydrochloric acid.

Dimethylarsine is a colorless, mobile liquid having the characteristic odor of cacodyl. It is very volatile and inflames in air at a temperature above 10° but not below 0°, burning with a blue-white arsenical flame and giving rise to white fumes and a black, solid deposit. It boils at 35°.6 (747 mm.) and at 55° under 1.74 atmospheres pressure.[1] Its sp. gr. is 1.213 at 29°.

The purity of the arsine used in the following studies is shown by the result of a molecular weight determination by Hofmann's method :

0.5794 gram $(CH_3)_2AsH$ gave 169 cc. vapor at 99°.3 and 750 mm.

[1] THIS JOURNAL, 33, 123.

	Calculated for $(CH_3)_2AsH$.	Found.
Mol. wt.	106.0	105.7

Like methylarsine,[1] dimethylarsine is soluble in alcohol, ether, chloroform, carbon bisulphide, benzene, etc., in all proportions. In fact, it resembles very closely the lower fatty primary arsines in their physical properties and most of their chemical reactions. In one particular it differs remarkably from the fatty primary arsines; whereas, the latter fume and inflame only on warming, dimethylarsine inflames spontaneously in the air, at a temperature almost as low as 0°. This same difference of ease of oxidation is seen also in the case of phenyl and diphenylarsines; the latter can be isolated only with the greatest difficulty by the method employed for the preparation of phenylarsine, on account of this great affinity for oxygen.

General Reactions of Dimethylarsine.

Dimethylarsine reacts with the greatest of ease with inorganic substances, such as the halogens, the halogen acids and their heavy metal salts, with oxygen and sulphur, with oxides and sulphides and with oxygenated acids and salts. Of the organic compounds affected by dimethylarsine, reactions with alkyl halides and reactions in which the arsines can exert a reducing effect have been studied the most. It may be said, in general, that only a few of the many reactions proposed and studied have failed to give definite transformations.

The reactions of the arsines may be divided into two general classes, *viz.*, those that involve

1. Addition,
2. Addition and subsequent dissociation,

or, in other words, reactions which involve a change from

1. Trivalent arsenic to pentavalent arsenic,
2. Pentavalent arsenic to trivalent arsenic.

Theoretically, all the reactions of the arsenic compounds may be explained on one or the other of these hypotheses.

[1] THIS JOURNAL, 33, 172.

With halogens, secondary arsines successively form compounds of the types $R_2AsH.X_2$, R_2AsX and R_2AsX_3, according to the equations:

$$R_2AsH + X_2 = R_2AsH.X_2 = R_2AsX + HX;$$
$$R_2AsX + X_2 = R_2AsX_3.$$

With halogen acids, either $R_2AsH.HX$ or R_2AsX, according to the equation:

$$R_2AsH + HX = R_2AsH.HX = R_2AsX + H_2.$$

With alkyl iodides, compounds of the types $R_2AsH.RX$, R_3As and R_4AsX, according to the equations:

$$R_2AsH + RX = R_3As.HX = R_3As + HX;$$
$$R_3As + RX = R_4AsX.$$

With halogen salts of the heavy metals, compounds of the type R_2AsX:

$$R_2AsH + MX_2 = R_2AsX + M + HX,$$

or, with the elimination of the halogen acid, compounds of the type R_2AsMX_n:

$$R_2AsH + MX_n = R_2AsMX_{n-1} + HX.$$

With the metalloids, such as sulphur, compounds of the types $(R_2As)_2S$ and $(R_2As)_2S_3$:

$$2R_2AsH + 2S = (R_2As)_2S + H_2S;$$
$$2R_2AsH + 3S = (R_2As)_2S_3 + H_2S.$$

With oxygen, compounds of the types $R_2As.AsR_2$, $R_2AsO.AsR_2$ and R_2AsOOH (*vide* oxidation of dimethylarsine, p. 9) and with oxygenated acids and salts, the oxidation products of arsine mentioned above, and the various reduction products of the acids and salts.

Method of Controlling Reactions.

On account of the spontaneous inflammability of dimethylarsine it was necessary to employ special methods for conducting and studying the reactions. The arsine, when prepared, was sealed in small bulbs or constricted test tubes. These

tubes were placed in ordinary bomb tubes, together with a heavy glass rod and the reagent, which was usually sealed in separate bulbs.

The bomb tubes were then constricted at the open end, cooled and filled with carbon dioxide passed in through capillary tubes, or, when ether was used as a medium for the reactions, the air contained in the bomb tubes was easily displaced by distilling out a portion of the ether. When filled with carbon dioxide or with ether vapor the tubes were sealed.

When slow regulated reactions were desired, or when danger of explosion was to be avoided, by careful agitation of the glass rod only the capillary tubes of the bulbs containing the arsine were broken.

Methods of Analysis.

In addition to the usual methods of analysis the following were employed:

Method (*a*). Analysis of many of the compounds containing halogen was greatly facilitated by the application of Volhard's method of titration. It was found that the halogen atoms linked directly to arsenic were easily removed by boiling with silver nitrate and nitric acid. The excess of silver nitrate used was titrated by means of thiocyanate, with ferric nitrate as an indicator. Preliminary analyses of arsenic trichloride, phenylarsine chloride and tetraethylarsonium iodide, by this method, gave quantitative results.

Method (*b*). Treatment of the substance with an excess of sodium peroxide[1] separated the arsenic from its organic groups and the former could be determined quantitatively by the usual methods.

Method (*c*). To determine the presence of inorganic arsenic, or the $RAs\equiv$ and $R_2As\equiv$ groups, the substance was first oxidized by chlorine or bromine water, then treated with magnesia mixture—a precipitate in the cold indicates inorganic arsenic (though possibly derived from RAs), a precipitate on boiling, the $RAs\equiv$ group; and a solution, which with zinc and hydrochloric acid evolves vapors having the fuming and

[1] THIS JOURNAL, 31, 386.

odor of the arsines, indicates the presence of R : As≡ group. In the presence of nitrates, chlorates, etc., the evolution of the arsines will often be retarded or suppressed.

Method (*d*). Another method for the detection of these constituents makes use of hydrogen sulphide, in hydrochloric acid solution ; a yellow, solid precipitate indicates inorganic arsenic; a slowly forming, light yellow, gummy oil[1] indicates RAs, and the immediate formation of a white emulsion or a colorless oil, $(R_2As)_2S$, indicates the presence of the R_2 : As≡ group.

Method (*e*). The presence of arsenic, either organic or inorganic, can be detected by treating with zinc and hydrochloric acid; the vapors evolved can usually be differentiated by the sense of smell.

Method (*f*). In gaseous mixtures the volume of arsenic present was determined by treatment with silver nitrate solution[2] (*vide* p. 34).

Decomposition of Dimethylarsine by Heat.

A bulb of 1.07 grams of dimethylarsine was sealed in a bomb tube (52 cc. capacity) from which the air was exhausted to 25 mm. pressure, and was then broken by the glass rod. A slight fuming indicated the presence of only a trace of air. The bomb tube was exposed to direct sunlight during 2 weeks[3] and was then heated for an hour at 192°, and for 2 hours at 242°, but no evident change took place. After the tube had been heated for an hour at 335°, it was found that the entire inner surfaces of the tube were covered by a beautiful, shining, black, metallic mirror. Upon opening the tube 46.6 cc. of gas were collected and treated with silver nitrate ; a decrease in volume of 10.1 cc. resulted, therefore 21.6 cc. of the gaseous products were unchanged arsine. The gas remaining after treatment with silver nitrate (36.5 cc.) burned with a blue flame and gave no easily explosive mixture with air—it was evidently methane or a mixture of ethane and hydrogen. The metallic deposit was washed with potassium hydroxide solution, then with water and dried at 122°.

[1] THIS JOURNAL, 33, 133.

[2] *Ibid.*, 33, 144.

[3] Cf. Arsine itself. J. prakt. Chem., 6, 346. Compt. rend., 93, 615. Ann. Chim. Phys., [5], 20, 20.

0.0430 gram was dissolved in bromine water and treated with magnesia mixture : 0.0829 gram $Mg_2As_2O_7$ resulted :

	Calculated for $(CH_3As)_x$.	Found.
As	82.63	83.33

This black, metallic, arsenic-like substance gave good tests for carbon, therefore it is evidently the black polymer mentioned by Auger,[1] and the reaction indicating the decomposition of dimethylarsine by heat is :

$$x(CH_3)_2AsH = (CH_3As)_x + xCH_4,$$

or

$$x(CH_3)_2AsH = (CH_3As)_x + \frac{x}{2}C_2H_6 + \frac{x}{2}H_2.$$

When arsine is heated to 230° it begins to decompose[2] and, at a red heat, is completely resolved according to the equation :[3]

$$2AsH_3 = 2As + 3H_2.$$

A more complete study of the decomposition of the arsines will be made during the year.

Oxygen and Dimethylarsine.

When dimethylarsine is treated with pure or atmospheric oxygen, any or all of the following reactions may take place :

1. $6(CH_3)_2AsH + 3O_2 = (CH_3As)_4.As_2O_3 + 4C_2H_6 + 3H_2O.$
2. $4(CH_3)_2AsH + O_2 = 4(CH_3As)_x + 2C_2H_6 + 2H_2O.$
3. $4(CH_3)_2AsH + O_2 = As_4 + 4C_2H_6 + 2H_2O.$
4. $2(CH_3)_2AsH + 9O_2 = As_2O_3 + 4CO_2 + 7H_2O.$
5. $4(CH_3)_2AsH + O_2 = [(CH_3)_2As]_2 + 2H_2O.$
6. $2(CH_3)_2AsH + O_2 = [CH_3)_2As]_2O + H_2O.$
7. $(CH_3)_2AsH + O_2 = (CH_3)_2AsOOH.$

When methylarsine[4] was treated with oxygen the following reactions occurred :

[1] Compt. rend., 138, 1707.
[2] Ber. d. chem. Ges., 22, 3202.
[3] Compt. rend., 93, 617. J. prakt. Chem., 6, 347. Ann. Chim. Phys., 43, 407.
[4] This Journal, 33, 124.

$$1.\ CH_3AsH_2 + O_2 = CH_3AsO + H_2O;$$
$$2.\ 2CH_3AsH_2 + 3O_2 = 2CH_3AsO_2H_2.$$

The following reactions of arsine[1] with oxygen have been reported:

$$1.\ 4AsH_3 + 3O_2 = 4As + 6H_2O;$$
$$2.\ 2AsH_3 + 3O_2 = As_2O_3 + 3H_2O.$$

Evidently *the affinity of the arsines for oxygen increases with the number of alkyl groups introduced;* for arsine itself does not unite, at ordinary temperatures, with oxygen, primary arsines do, but not with the spontaneous inflammability which characterize the secondary and tertiary arsines.

All of the above oxidation products of dimethylarsine, except cacodyl, have been identified. On account of its spontaneous inflammability, it has been found impossible to isolate it from the oxidation product, however, since it is often found as a product of oxidation when liquid oxidizing agents are employed, it is easy to see that it is probably formed when gaseous arsine is treated with diluted oxygen or mild oxidizers.

When dimethylarsine is permitted to oxidize slowly in the air, there is always formed a bright red solid, which is probably identical in composition with "erytrarsine" described by Bunsen,[2] whose data indicate a compound of the formula

$$(CH_3As)_4.As_2O_3.$$

Evidence for the presence of the loosely bound inorganic arsenious oxide and of the CH_3As group is seen in the following. The substance was washed repeatedly with water and then with alcohol, to remove any adhering cacodylic acid or cacodylic oxide and was then dissolved in bromine water; upon making ammoniacal and adding magnesia mixture a copious precipitate of NH_4MgAsO_4 was obtained.

After filtering, acidifying with hydrochloric acid and treating with hydrogen sulphide there was formed a precipitate of

[1] Ann. Chim. Phys., **33**, 355; **43**, 407. J. prakt. Chem., **6**, 347. Comment. Soc. Gött., **16**, 141. Ber. d. chem. Ges., **22**, 3203.

[2] Ann. Chem. (Liebig), **42**, 41.

CH_3AsS_2, recognized by its oily consistency and its characteristic odor.[1]

When dimethylarsine is treated with pure oxygen, or when warmed and treated with concentrated oxygen, the reaction gives rise to a flame and the immediate formation of a black solid, which has been proved to be a mixture of $(CH_3As)_x$[2] and metallic arsenic. Evidence for the presence of the CH_3As grouping was derived in the manner described above for the red polymer. In fact this black polymer can be obtained from the red polymer by heating.[3] The red and black polymers are insoluble in dilute alkalies; the solid resulting from the flame reaction can be proved to contain arsenious acid, by dissolving in dilute alkalies and testing in the usual manner.

Proof of the formation of metallic arsenic[4] was obtained as follows: When liquid arsine was dropped into pure oxygen a closely compacted, metallic mirror was formed. On removing and washing it free from cacodylic acid it was found to give no test for carbon, but gave all of the usual tests for metallic arsenic.

The formation of ethane was proved thus: The gas resulting from a flame reaction was obtained in a eudiometer over mercury and treated, successively, with alkaline pyrogallol to remove oxygen, with silver nitrate to remove unchanged arsine, and with bromine water to remove unsaturated hydrocarbons (such have not been found). The residual gas was found to burn with quite a luminous flame and to give no deposit of metallic arsenic on cold porcelain. When 11.8 cc. of the residual gas, known to contain nitrogen, were treated with 4.98 cc. of oxygen and exploded in a mercury pipette, a contraction of 2.92 cc. resulted, owing to the formation of water. After treating with potash a further contraction of 2.28 cc. was incurred. According to the equation

$$2C_2H_6 + 7O_2 = 4CO_2 + 6H_2O,$$

[1] Ber. d. chem. Ges., 16, 1441. THIS JOURNAL, 33, 134. Ann. Chem. (Liebig), 249, 134.

[2] Compt. rend., 138, 1707.

[3] Cf. Ann. Chem. (Liebig), 42, 42. Compt. rend., 138, 1707.

[4] Cf. Primary Arsines. THIS JOURNAL, 33, 124.

the contraction owing to the formation of water is to the contraction owing to the formation of carbon dioxide, as 5 : 4. The ratio found was 2.92 : 2.28, that is, an error of 2 per cent.

The gas resulting from the flame reaction can easily be proved to contain carbon dioxide by passing it through lime water.

In the flame reaction and in all other oxidations of dimethylarsine, cacodylic acid and usually cacodylic oxide can easily be proved to be present in the products. The former was separated by dissolving in water or alcohol and was identified by its crystalline form and melting-point; the latter was detected by its solubility in water and its characteristic, penetrating odor—all of the other substances mentioned above are practically odorless.

It may be said, in general, that cacodylic acid and cacodylic oxide are products of slow oxidation. The former is almost the total product when an ether solution is exposed, through a small orifice, to the action of the air; the latter is abundant when air and arsine are brought together in the presence of water. In either case some of the red polymer mentioned previously may be formed.

Further evidence in proof of the above 7 oxidation reactions is derived from gasometric studies. The following tables give the volumes of arsine and oxygen required by these 7 equations, the resulting volumes and contractions are given in per cents of the arsine and oxygen used.

Equation.	Arsine.	Oxygen.	Resulting.	Per cent of contraction of the Arsine.	Oxygen.
1	6	3	4	83	166
2	4	1	1	100	400
3	4	1	4	25	100
4	2	9	4	350	77
5	4	1	0	125	500
6	2	1	0	150	300
7	1	1	0	200	200

The following reactions were conducted in a nitrometer containing mercury and surrounded by a jacket, through which were passed the vapors of chloroform. All data given below

have been calculated to standard conditions of temperature and pressure :

Experiment.	Arsine.	Oxygen.	Resulting.	Contractions.	Per cent of contraction to arsine.
(*a*)	17.36	43.51	44.90	15.97	0.92
(*b*)	22.77	32.71	27.77	27.71	1.22
(*c*)	20.29	34.37	44.43	30.23	1.49

In experiment (*a*) a strong flame-reaction resulted, while in (*b*) less, and in (*c*) little flame-reaction was observed. Evidently a combination of reactions (2), (3), (6) and (7) with none of (2) and (3) in experiments (*a*) and (*b*), and none of (6) and (7) in (*c*). Further evidence for these conclusions was derived from a study of the oxidation products ; no red polymer, carbon dioxide, or cacodyl was found in experiments (*a*), (*b*) or (*c*), therefore reactions (1), (4) and (5) are eliminated ; the black polymer, cacodylic oxide and cacodylic acid were found, therefore, necessarily, combinations of (2), (3), (6) and (7) were involved.

When reactions with oxygen, without the flame-reaction, take place, invariably contractions equal in volume to 150–200 per cent of the arsine result ; evidently only reactions (6) and (7) are involved under these conditions.

In the following experiments a mixture of hydrogen and arsine was prepared, kept in a suitable gas reservoir, and its per cent of arsine determined by treatment with a solution of silver nitrate.

Quantities of the mixture were drawn off into Hempel burettes, measured and treated, either rapidly or slowly, with measured quantities of air ; fuming but no flame-reaction resulted ; slightly greater contractions were observed upon rapid treatment.

No. of experiment.	Mixture.	Air.	Sum.	Result.	Contraction.	Corrected volume of arsine.	Per cent of contraction of arsine.
1	21.2	69.2	90.4	72.6	17.8	10.6	168
2	26.6	79.8	106.4	84.6	21.8	13.3	164
3	18.6	78.6	97.2	82.1	15.1	9.3	162
4	29.2	75.0	104.2	79.0	25.2	14.6	172
5	16.7	75.0	91.7	77.2	14.5	8.3	174
6	16.0	80.1	96.1	82.2	13.9	8.0	174

Evidently treatment with atmospheric oxygen gives, as products, approximately equal quantities of cacodylic oxide and cacodylic acid.

Halogens and Dimethylarsine.

When halogens are brought into contact with gaseous or liquid dimethylarsine, there result immediate energetic reactions attended by light, if no diluent is employed; when organic diluents are used, precipitates of the pentavalent addition products are formed, according to the equation:

$$R_2AsH + X_2 = R_2AsX.HX.$$

However, when water is present or the temperatures are too high, the addition products dissociate into trivalent arsenic halides:

$$R_2AsHX_2 = R_2AsX + HX;$$

thus the products of the action of halogens on dimethylarsine are cacodyl halides or their hydrhalogen salts, except when the halogen is permitted to react at very high temperatures, then flame-reactions take place and there result polymerized or decomposed products similar to those formed by reactions 2, 3 and 4 of oxidation.

Bromine and Dimethylarsine.

When 5.5 grams of dimethylarsine (1 mol.) and 9 grams of bromine (excess of 1 mol.) were brought together in a sealed tube, so that an energetic reaction took place, there resulted a solid mass of dark brown color and a little colorless oil. On standing for some time the solid changed to large, white, tabular crystals and a little dark brown, amorphous solid. On opening the tube considerable pressure was noticed, the gaseous products were collected and were proved to contain hydrobromic acid and hydrogen. The former was identified by absorption in potassium hydroxide solution and treatment with silver nitrate, the latter by its combustibility. To prove the presence of hydrogen, 2.3 cc. of the gas, freed from hydrobromic acid, was exploded with oxygen; a contraction of

3.6 cc. resulted, an error of 3 per cent. The colorless oil was drained from the crystals, filtered and analyzed for halogen:

0.3393 gram substance required 0.4006 gram silver nitrate.

	Calculated for $(CH_3)_2AsHBr_2$.	Calculated for $(CH_3)_2AsBr$.	Found.
Br	60.20	43.24	55.57

Evidently the oil was a mixture of cacodyl bromide and *bromcacodyl hydrobromide*; upon standing, crystals of the latter were deposited.

The white crystals, the main product of the action of bromine upon dimethylarsine, were washed with chloroform, separated mechanically from the broken glass and the brown, amorphous solid, dried in a desiccator and analyzed by Volhard's titration method.

I. 0.1508 gram substance required 0.2599 gram $AgNO_3$.
II. 0.0618 gram substance required 0.0791 gram $AgNO_3$.

	Calculated for $(CH_3)_2AsBr.HBr$.	Found. I.	Found. II.
Br	60.20	60.52	60.26

Bromcacodyl hydrobromide, a white, tabular, crystalline solid, is quite stable in air. It is somewhat soluble in hot chloroform, less so in carbon bisulphide, and is insoluble in ether. It decomposes slowly in cold water and rapidly in hot water and ammonium hydroxide, according to the equation:

$$(CH_3)_2AsBr.HBr = (CH_3)_2AsBr + HBr.$$

When 6.2 grams of dimethylarsine (1 mol.) and 10 grams of bromine (1 mol.) were brought into contact and their reaction products were immediately decomposed by means of water and then subjected to steam distillation, 2.5 grams of cacodyl bromide were separated.

After removing the cacodyl bromide there was left a dark brown, amorphous solid, which was probably identical with Bunsen's "erytrarsine" mentioned above. After boiling repeatedly with water, and drying at 120°, it was analyzed for arsenic.

0.2138 gram substance gave 0.2358 gram $Mg_2P_2O_7$.

	Calculated for $(CH_3As)_4.As_2O_3$.	Calculated for $(CH_3As)_x$.	Found.
As	80.64	83.33	82.10

The above data justify the following equations to represent the reaction when dimethylarsine is brought into contact with bromine :

$$(CH_3)_2AsH + Br_2 = (CH_3)_2AsBr.HBr;$$
$$(CH_3)_2AsH.HBr = (CH_3)_2AsBr + HBr;$$
$$(CH_3)_2AsH + HBr = (CH_3)_2AsBr + H_2 \text{ (}\textit{vide}\text{ p 22).}$$

The formation of the polymer is cleared up by a study of the action of arsenic trichloride upon dimethylarsine (*vide* p. 40).

Chlorine and Dimethylarsine.

A quantity of dimethylarsine was placed in a gas wash bottle and treated with a slow stream of dry chlorine ; an immediate flame-reaction took place, attended by a deposition of arsenic and of a black solid polymer. When an excess of chlorine was added, the reaction product became chiefly liquid. The contents of the wash bottle were extracted with chloroform and its solution was dried and distilled. Methylarsine dichloride, CH_3AsCl_2, was found to be the chief constituent of the liquid which boiled at 100°–150° (CH_3AsCl_2 boils at 123° ; $(CH_3)_2AsCl$ boils at 100°). The fraction boiling at 140°-145° was analyzed for chlorine :

0.1948 gram substance required 0.4208 gram $AgNO_3$.

	Calculated for $(CH_3)_2AsCl$.	Calculated for CH_3AsCl_2.	Found.
Cl	24.93	44.10	44.98

It is probable that chlorine reacted with dimethylarsine, as did bromine, with the formation of *chlorocacodyl hydrochloride*,

$$(CH_3)_2AsH + Cl_2 = (CH_3)_2AsCl.HCl,$$

which decomposed at the temperature of the reaction and formed cacodyl chloride,

$$(CH_3)_2AsH.HCl = (CH_3)_2AsCl + HCl.$$

Cacodyl chloride could then react with chlorine according to

the known reaction and form the pentavalent body, dimethylarsine trichloride,

$$(CH_3)_2AsCl + Cl_2 = (CH_3)_2AsCl_3,$$

which decomposes at a temperature above 40°–50°, and forms methylarsine dichloride and methyl chloride,[1]

$$(CH_3)_2AsCl_3 = CH_3AsCl_2 + CH_3Cl.$$

The phenomenon attending the reaction of the chlorine with arsine is very similar to that with dimethylarsine.[2]

Iodine and Dimethylarsine.

When 2.6 grams of dimethylarsine (1 mol.) were treated in a sealed tube with 6.2 grams of iodine (1 mol.), an immediate reaction took place, with the liberation of much heat and the formation of a yellow solid, which crystallized on standing. Little or no pressure was observed on opening the tube. By washing with chloroform the crystalline substance, *iodocacodyl hydriodide*, $(CH_3)_2AsI.HI$, was obtained pure. It crystallizes in large, well-formed, light yellow needles which, when heated rapidly, soften and darken at 160°, and melt at 175°; by continued heating at 60° the crystals darken and liberate iodine. Iodocacodyl iodide is insoluble in ether and chloroform and soluble in alcohol, with evident decomposition. Water decomposes it easily, according to the equation:

$$(CH_3)_2AsI.HI = (CH_3)_2AsI + HI.$$

0.1244 gram substance required 0.1299 gram $AgNO_3$.

	Calculated for $(CH_3)_2AsI.HI$.	Found.
I	70.55	69.90

Iodine decomposes arsine slowly in the cold, rapidly on heating, into hydriodic acid and arsenic trioxide.[3]

Aqueous Iodine and Dimethylarsine.

When 0.1848 gram of dimethylarsine was brought into contact with an excess of standard iodine solution and the un-

[1] Ann. Chem. (Liebig), 107, 269.

[2] Ann. Chim. Phys. [2], 43, 407. Gmelin-Kraut Handbuch der Chemie.

[3] Ann. Chim. Phys., [2], 43, 407. Compt. rend., 67, 56. Anal. Zeitschr., 7, 476. Ber. d. chem. Ges., 20, 1099; 21, 2546.

changed iodine titrated with standard thiosulphate solution, the following reaction was found to have taken place:

$$(CH_3)_2AsH + 4I + 2H_2O = (CH_3)_2AsOOH + 4HI.$$

0.8716 gram of arsine was used, whereas the theory required 0.8916 gram—the error of 2 per cent being accounted for by the difficulty of avoiding oxidation.[1]

Alkyl Halides and Dimethylarsine.

In 1854 Landolt[2] found that triethylarsine reacted with ethyl iodide, slowly in the cold, more rapidly when heated, and formed a crystalline product, tetraethylarsonium iodide, $(C_2H_5)_4AsI$. This reaction was found to be analogous to the formation of tetramethylstibonium iodide, $(CH_3)_4SbI$, from trimethylstibine and methyl iodide.[3] It was observed by one of us[4] that when primary arsines were heated with 3 molecules of alkyl iodides, there resulted arsonium iodides of the types RR'_3AsI and R_4AsI.[5] It was stated that the intermediate products $RR'AsH.HI$ and $RR'_2As.HI$ were probably formed, but, being unstable, split off hydriodic acid and added more alkyl iodide, until the arsonium body was produced. We have found that the secondary arsines react with equal ease with the alkyl iodides, forming both the intermediate product $R_2R'As.HI$ and the end product, the arsonium iodide, according to whether the arsine is allowed to react with 1 molecule of the alkyl iodide in the cold or is heated with 2 molecules:

$$R_2AsH + R'I = R_2R'As.HI;$$
$$R_2AsH + 2R'I = R_2R'As.R'I + HI.$$

Dimethyldiisobutylarsonium Iodide.

When 5 grams of dimethylarsine were sealed with 21.7 grams of isobutyl iodide (2.5 mols.) and heated 5 hours, at 110°, there resulted a crystalline mass, colored red by a small amount of arsonium periodides. The solid was extracted from the reaction tube by means of water and heated in a beaker,

[1] Cf. Primary Arsine. THIS JOURNAL, 33, 126.
[2] Ann. Chem. (Liebig), 89, 331.
[3] *Ibid.*, 84, 44.
[4] THIS JOURNAL, 33, 128.
[5] *Ibid.*, 33, 115.

on the water-bath, with potassium hydroxide solution, to destroy the periodides and to evaporate the excess of alkyl iodides used. The arsonium iodide separated from the alkali solution as a solid and was removed by filtering on glass wool. It was extracted from the glass wool by means of chloroform and, after drying with calcium chloride, was precipitated by ether as a white, crystalline solid. It is soluble in alcohol and chloroform, but insoluble in ether and melts at 155°.

0.2470 gram substance required 0.1213 gram $AgNO_3$.

	Calculated for $(CH_3)_2(C_4H_9)_2AsI$.	Found.
I	36.70	36.67

Dimethyldicetylarsonium Iodide.

Dimethylarsine (5.94 grams) did not react with 49.3 grams of cetyl iodide (2 mols.) on standing at room temperature. After heating 5 hours, at 100°, the entire mass was changed to a crystalline solid.

The solid was decolorized by boiling with potassium hydroxide, which precipitated it as an oil. It was separated from the alkali solution and dissolved in chloroform. The dry chloroform solution was diluted with much ether and cooled, when the dimethyldicetylarsonium iodide separated as a slightly yellow, crystalline solid. It was obtained perfectly white on recrystallizing. It melts at 53°–54°.

0.1872 gram substance required 0.0465 gram $AgNO_3$.

	Calculated for $(CH_3)_2(C_{16}H_{33})_2AsI$.	Found.
I	18.62	18.57

Dimethyldiisopropylarsonium Iodide.

Dimethylarsine (4.6 grams) and isopropyl iodide (18 grams, 2.5 mols.), after standing in contact 18 hours, deposited some crystals; after heating for 3 hours, at 100°, the entire mass became solid. The arsonium iodide, freed from arsonium periodides by boiling with potassium hydroxide, was precipitated from the chloroform solution by ether, in the usual manner.

Dimethyldiisopropylarsonium iodide is a pure white, crystalline solid easily soluble in chloroform and very insoluble in ether. It does not melt at 230°.

0.1136 gram substance required 0.0604 gram $AgNO_3$.

	Calculated for $(CH_3)_2(C_3H_7)_2AsI$.	Found.
I	39.93	39.68

Dimethyldiallylarsonium Iodide.

A large excess of allyl iodide (3–4 mols.) reacted very violently with dimethylarsine, liberating sufficient heat to boil the mixture. A precipitate began to form and in less than 30 minutes the entire mass had become solid. On opening the tube in which the reactions had taken place much pressure was observed; vapors of iodine, hydriodic acid, and a gas that burned with a sooty flame were given off. On account of the large excess of allyl iodide it was impossible to separate the arsonium iodide in the usual manner, but crystals dried on clay plates were found to be light yellow in color, soluble in alcohol and insoluble in ether. Analysis:

0.1330 gram substance required 0.0709 gram $AgNO_3$.

	Calculated for $(CH_3)_2(C_3H_5)_2AsI$.	Found.
I	40.44	39.81

Dimethylallylarsine.

When dimethylarsine (3 grams) was treated with 1 molecule of allyl iodide (4.8 grams) the reaction was not so violent as when 3 to 4 molecules of the allyl iodide were used in the preparation of dimethyldiallylarsonium iodide. As the arsine was slowly added a yellow precipitate was first formed, but it disappeared when all of the arsine came into contact with the reaction mixture. Only a little heat was evolved. On opening the tube a pressure due to hydriodic acid was observed; arsine was absent. The liquid contents were removed and distilled. ***Dimethylallylarsine*** distilled at about 160° and yielded a clear, light yellow, non-fuming liquid of a strong, disagreeable odor, irritating to the eyes and skin. It was proved to be a tertiary arsine by treatment with 1 molecule of methyl iodide. Crystals

formed at ordinary temperatures; when heated 1 hour at 75°–80° the entire mass became solid, owing to the production of the trimethylallylarsonium iodide, $(CH_3)_3(C_3H_5)AsI$. Dimethylallylarsine reacted violently with bromine, in ether solution, and formed a yellow, flocculent precipitate, ***dimethylallylarsine dibromide***, $(CH_3)_2(C_3H_5)AsBr_2$.

Alkalinity of the Arsines.

It was stated by one of us[1] that the primary arsines possess weakly basic properties. We have found that the secondary arsines also possess basic properties; they form, with sulphuric acid, well-defined, crystalline salts which are unstable in moist air; with halogen acids, salts which are decomposed at ordinary temperatures; and with platinic chloride, double salts which are analogous in composition to the corresponding amines. The equation for the formation and decomposition of the sulphuric acid salt is as follows:

$$2(CH_3)_2AsH + H_2SO_4 \rightleftarrows [(CH_3)_2AsH]_2H_2SO_4.$$

The formation and decomposition of the halogen acid compounds are represented thus:

$$(CH_3)_2AsH + HX = (CH_3)_2AsH.HX;$$
$$(CH_3)_2AsH.HX = (CH_3)_2AsX + H_2.$$

The compounds produced with platinic chloride are

$$[(CH_3)_2AsH]_2.H_2PtCl_6 \text{ and } (CH_3)_2As.H_2PtCl_6.$$

We have found that the tertiary arsines also possess basic properties. This is best seen in the action of alkyl halides upon dimethylarsine,

$$(CH_3)_2AsH + RI = (CH_3)_2RAs.HI.$$

This hydriodic acid salt of the tertiary arsine is quite stable in dry air, but is decomposed by water according to the equation:

$$(CH_3)_2RAs.HI = (CH_3)_2RAs + HI.$$

In the aromatic series tertiary arsines have been found to

[1] THIS JOURNAL, 33, 111.

have some basic properties; Michaelis prepared triphenylarsine hydroplatinic chloride,[1]

$$[(C_6H_5)_3As]_2H_2PtCl_6.$$

Dry Hydrobromic Acid and Dimethylarsine.

A bulb of dimethylarsine was placed in a small bottle and the whole was weighed. It was then connected on both sides with U-tubes containing phosphorus pentoxide; to one drying tube was attached an apparatus for the generation of gaseous hydrobromic acid; to the other U-tube, small wash bottles containing solutions of potassium hydroxide and silver nitrate, respectively. The silver nitrate wash bottle was connected to a Hempel burette for the collection of gas.

The bottle containing the bulb of arsine was surrounded by a freezing mixture (—10°) and dry carbon dioxide was passed through the apparatus until the air was displaced. After breaking the arsine bulb by means of a glass rod inserted through the cork of the bottle, a stream of pure, dry hydrobromic acid was passed through the apparatus. Absorption in the arsine was noticeable, although unchanged arsine and hydrobromic acid contributed a steady stream of outgoing gas, which was completely soluble in the wash bottles containing the potassium hydroxide and silver nitrate solutions. After some time the bottle containing the reaction mixture was detached and was found to have increased largely in weight, though, of course, not quantitatively, according to the equation

$$(CH_3)_2AsH + HBr = (CH_3)_2AsH.HBr.$$

In another experiment the bottle containing the arsine was not detached, but the freezing mixture was removed and the contents of the bottle were permitted to warm to the room temperature. A marked change took place in the composition of the gas evolved; only a little arsine, but much hydrogen was collected. The latter was identified in the usual manner. The liquid remaining in the bottle was dissolved in water, treated with hydrogen sulphide and was proved to be cacodyl

[1] Ann. Chem. (Liebig), 321, 161.

bromide. Therefore, at —10° to 20°, ***dimethylarsine hydrobromide*** is decomposed as follows:

$$(CH_3)_2AsH.HBr = (CH_3)_2AsBr + H_2.$$

Aqueous Hydrobromic Acid and Dimethylarsine.

When 1.95 grams of dimethylarsine (1 mol.) were treated, in a sealed tube, with 4 grams of a 45 per cent solution of hydrobromic acid (excess of 1 mol.) no reaction was observed even after standing for 2 months; the arsine remained undissolved as an upper layer. Opon opening the tube in connection with a Hempel burette, no gas was given off, but it was found that the contents of the tube fumed in the presence of air. The same conditions were observed even after heating to 95° for 1 hour; but after heating to 125° for 24 hours a quantity of hydrogen equal to more than one-half of the hydrogen in the original 1.95 grams of arsine was collected; the liquid contents of the tube fumed only slightly on being exposed to the air; by its odor and immediate precipitation with hydrogen sulphide it was easily proved to contain cacodyl bromide. Thus the reaction with a solution of hydrobromic acid, at an elevated temperature, is as follows:

$$(CH_3)_2AsH + HBr = (CH_3)_2AsBr + H_2.$$

Dry Hydriodic Acid and Dimethylarsine.

Dimethylarsine was treated with dry hydriodic acid as with dry hydrobromic acid. Their contact at room temperature was attended by an evolution of heat and the formation of a white, crystalline mass, which soon began to effervesce and to be transformed into a light yellow liquid, this, by its odor and immediate precipitation from an aqueous solution by hydrogen sulphide, was identified as cacodyl iodide. The rapidity of the decomposition of the dimethylarsine hydriodide, according to the equation

$$(CH_3)_2AsH.HI = (CH_3)_2AsI + H_2,$$

made it impossible to isolate it for study or for analysis. However, a determination was made of the amount of hydrogen evolved by a given amount of dimethylarsine:

0.6248 gram dimethylarsine gave 150.5 cc. hydrogen at 747 mm. and 25° = 0.01175 gram H_2.

Theoretically, 0.648 gram of dimethylarsine gives 0.01175 gram of hydrogen. Therefore, dimethylarsine was nearly quantitatively transformed into cacodyl iodide and hydrogen, by the action of hydriodic acid, according to the equation:

$$(CH_3)_2AsH + HI = (CH_3)_2AsH.HI = (CH_3)_2AsI + H_2.$$

Parsons[1] found that arsine itself is not acted upon by halogen acids, in aqueous solutions. Janowsky and Napoli,[2] however, found that it reacts with dry hydrochloric acid. From consideration of the above reactions it seems very probable that both dry halogen acids and their aqueous solutions will react with arsine, at sufficiently high temperatures.

Sulphuric Acid and Dimethylarsine.

When 6.6 grams of dimethylarsine and 4.5 grams of sulphuric acid (sp. gr. 1.84) were brought into contact, in a sealed tube containing carbon dioxide, heat was produced at the planes of contact. After standing for some time the contents of the tube separated into liquid layers, a heavy white oil and a lighter liquid of a pale yellow color. Heating 3 hours increased the volume of the lower layer.

Large, colorless, prismatic crystals slowly formed in the lower layer, the whole of which became solid at —16°. Some of these crystals were removed, dried on a clay plate over sulphuric acid, and analyzed:

0.0979 gram substance gave 0.0706 gram $BaSO_4$.

	Calculated for $[(CH_3)_2AsH]_2H_2SO_4$.	Found.
S	10.32	9.90

Dimethylarsonium sulphate decomposes slowly in air, and rapidly in water, forming sulphuric acid and arsine.

Cacodylic acid proved to be present in the lower layer of the reaction products. By adding water to a portion of it and boiling so as to exclude the air, all arsine passed off, leaving a clear solution that yielded the usual tests for cacodylic acid.

[1] Chem. News, 35, 236.

[2] Ber. d. chem. Ges., 6, 220; 8, 1637. Sill. Am. J., [2], 18, 190.

The yellow oil constituting the upper layer (3 grams) was separated and distilled. It was found to boil at 210°–213° (cacodylic sulphide boils at 211°) and possessed the peculiar odor of cacodylic sulphide. Equations indicating the formation of cacodylic sulphide and cacodylic acid are as follows:

$$2(CH_3)AsH + H_2SO_4 = [(CH_3)_2As]_2S + 2H_2O + O_2;$$
$$(CH_3)_2AsH + O_2 = (CH_3)_2AsOOH.$$

When dimethylarsine is passed through sulphuric acid for some time, as in the case of the sulphuric acid contained in the wash bottle beyond the condenser in the preparation of dimethylarsine, a copious precipitate of arsine trisulphide is produced. Too little data is available to explain its formation. Sulphuric acid is reported to have no effect on arsine.[1]

The Oxides of Nitrogen and Dimethylarsine.

All of the oxides of nitrogen, except nitrous oxide, attack dimethylarsine at ordinary temperatures and are reduced to nitrous oxide or nitrogen, while the arsine itself is variously oxidized, cacodylic acid being the most abundant product.

Nitrous Oxide and Dimethylarsine.

When 38.6 cc. of a mixture of hydrogen and dimethylarsine, containing 20 per cent of the latter, were treated with 41.4 cc. of nitrous oxide, no evident reaction resulted after standing 5 minutes, at the ordinary temperature. After washing with water to remove the nitrous oxide, the gas was treated with silver nitrate solution; there resulted a precipitation of silver and a contraction equal in volume to that of the arsine present in the original mixture, therefore, nitrous oxide has no effect on dimethylarsine at ordinary temperatures.

Nitric Oxide and Dimethylarsine.

When a mixture of hydrogen and dimethylarsine was treated with an excess of nitric oxide, the resulting mixture did not fume in the air nor precipitate with silver nitrate; therefore, the arsine was completely oxidized. When an excess of arsine was used the resulting gas did not become brown

[1] Ber. d. chem. Ges., 16, 2947; 17, 209, 377, 674. Z. anal. Chem., 22, 147; 23, 148.

on mixing with air, hence, the nitric oxide was completely reduced. In both cases a clouding and an odor suggestive of cacodylic oxide were manifest. When 73.7 cc. of nitric oxide were treated in a mercury burette, with 44.6 cc. of a mixture of hydrogen and dimethylarsine, containing 20 per cent of the latter, a contraction of 15.3 cc., equal to nearly twice the volume of arsine involved, resulted. All of the data are best expressed by the following equation:

$$2(CH_3)_2AsH + 4NO = [(CH_3)_2As]_2O + H_2O + 2N_2O.$$

Nitrous Acid and Dimethylarsine.

When 0.79 gram of dimethylarsine (1 mol.) was treated in a sealed tube, filled with carbon dioxide, with 2 grams of potassium nitrite (4 mols.) and an excess of hydrochloric acid (6 mols.) contained in 50 cc. of water, an immediate reaction took place; heat was generated and a yellow-white opacity was imparted to the solution. On opening the tube 99.8 cc. of gas were collected and analyzed; it yielded 26 per cent of carbon dioxide, 11 per cent of unchanged arsine and 63 per cent of a gas which gave a good test for nitrous oxide, but may also have contained free nitrogen. The aqueous solution in the tube was proved to contain unchanged dimethylarsine, cacodyl, cacodylic acid and a little cacodylic chloride. Evidently the main reaction was:

$$(CH_3)_2AsH + 2HNO_2 = (CH_3)_2AsOOH + N_2O + H_2O.$$

When Parsons[1] treated arsine with nitrous acid he obtained the following reaction:

$$12KNO_2 + 6H_2SO_4 + 2AsH_3 = As_2O_3 + 12NO + 6K_2SO_4 + 9H_2O.$$

Nitrogen Tetroxide and Dimethylarsine.

Dimethylarsine and liquid nitrogen tetroxide, in equal molecular proportions, contained in small bulbs, were sealed in a tube filled with carbon dioxide. The dimethylarsine bulb was first broken and then the tip of the capillary of the nitrogen tetroxide bulb, so that the oxide distilled slowly into the

[1] Chem. News, 38, 235.

vapors of the dimethylarsine. An intense flame-reaction resulted and sufficient heat was liberated to melt the sealed tube at the point of the reaction. A black metallic deposit, a white solid, and a little liquid resulted. On opening the tube great pressure was observed; the gas was proved to contain nitrogen, but none of its lower oxides. Unchanged arsine, cacodyl, cacodylic acid (0.3 gram acid—theory 2.3 grams) and the black polymer were identified as the oxidation products. The last-mentioned compound probably results from the heat (cf. p. 9) of the following reactions:

$$2(CH_3)_2AsH + N_2O_4 = 2(CH_3)_2AsOOH + N_2;$$
$$8(CH_3)_2AsH + N_2O_4 = 4[(CH_3)_2As]_2 + N_2 + 4H_2O.$$

Action of Nitric Acid on Dimethylarsine.

When 0.83 gram of dimethylarsine (1 mol.) was treated, in a sealed tube, with 1.4 grams of nitric acid (2 mols.), contained in 30 cc. of water, no evident reaction was manifest, even after heating for 1 hour, at 125°. However, when 0.69 gram of dimethylarsine (1 mol.) and 5 cc. of concentrated nitric acid (23 mols.) were brought together in a sealed tube, filled with carbon dioxide, an energetic reaction resulted; red and black polymers were formed, while a flame and much heat were produced. The gaseous contents of the tube were colored brown by the presence of nitrogen peroxide; 82.1 cc. were collected and washed with water (loss 8.9 cc.), then with potassium hydroxide (loss 22.5 cc.); the residual gas proved to be nitrogen. The liquid contents of the tube were found to contain arsenic acid, cacodylic acid, and a little gray substance which was insoluble in water and nitric acid. Here, as with nitrogen tetroxide, the formation of the polymers may be due to the heat of the reactions:

$$(CH_3)_2AsH + 4HNO_3 = (CH_3)_2AsOOH + 4NO_2 + 2H_2O;$$
$$5(CH_3)_2AsH + 4HNO_3 = 5(CH_3)_2AsOOH + 2N_2 + 2H_2O.$$

Evidently other reactions are necessary to account for the arsenic acid and the insoluble substance.[1]

[1] Cf. Primary Arsines. THIS JOURNAL, 33, 125, 144.

Chromic Acid and Dimethylarsine.

An aqueous solution of 1 gram (4 mols.) of chromic anhydride was treated, in a sealed tube, with 0.91 gram of dimethylarsine (3 mols.). An immediate reaction was observed, the yellow of the chromic acid solution being changed gradually, during 24 hours, to a deep yellow solution and there being precipitated a dirty green solid, with a few heavy, oily drops. After 2 months the tube was opened; the gaseous portion and the oily drops were found to fume. This fuming, its odor and boiling point, proved the oil to be cacodyl and not unchanged arsine. The dirty green precipitate was washed successively, with water, alcohol and ether, then dried at 100° and identified, by its loss in weight, as chromium hydroxide. By ignition 0.0437 gram gave 0.0323 gram or a loss of 26 per cent. Chromium hydroxide loses 26.09 per cent.

The green solution was filtered, treated with an excess of ammonia, boiled and filtered free from chromium hydroxide. After evaporating on the water-bath crystals of cacodylic acid were found. Therefore, dimethylarsine is oxidized by chromic acid as follows:

$$6(CH_3)_2AsH + 2H_2CrO_4 = 3[(CH_3)_2As]_2 + 2Cr(OH)_3 + 2H_2O;$$

$$3(CH_3)_2AsH + 4H_2CrO_4 + 2H_2O = 3(CH_3)_2AsOOH + 4Cr(OH)_3$$

It will be observed that an excess of chromic acid is favorable to the formation of cacodylic acid, while small quantities of chromic acid oxidize the arsine to the cacodyl stage only.

Parsons reports that chromic acid has no effect on arsine itself.[1]

Potassium Bichromate and Dimethylarsine.

When a mixture of dimethylarsine and hydrogen is treated in a Hempel burette, with excess of an aqueous solution of potassium bichromate, a loss in volume equal to the arsine present is produced. For instance, when such a gaseous mixture, known to contain 21.7 per cent of arsine, was treated in this

[1] Chem. News, 35, 236.

manner, two determinations gave losses of 21.5 per cent and 21.7 per cent, respectively. When the arsine comes into contact with the potassium bichromate, an immediate darkening of the latter is observed and there is precipitated an amorphous solid of a brown-red color. When 0.67 gram of dimethylarsine (1 mol.) was treated, in a sealed tube, with 3 grams of potassium bichromate (nearly 2 mols.) an immediate brown-black darkening of the solution was observed. Upon opening the tube the odor of arsine had disappeared. The brown-red precipitate was filtered, washed and dried at 100°. Upon igniting, 0.0301 gram of this solid and 0.0223 gram of a dark green solid resulted.

According to the equation[1]

$$2CrO_3.H_2O = Cr_2O_3 + O + 2H_2O,$$

there should result 0.0222 gram of chromium trioxide.

Molybdic Acid and Dimethylarsine.

When 2.13 grams of dimethylarsine (1 mol.) were treated, in a sealed tube, with 6 grams of molybdic acid (2 mols.) and 25 cc. of water, a slow reaction was noticed—the white, insoluble acid gradually, during 1–7 days, changed through slate, green-white and blue, to a blue-black color. On opening the tube no odor of arsine was detected; the clear, aqueous solution gave, by evaporation, well formed crystals of cacodylic acid. The precipitate, when wet by liquids, possessed a beautiful, iridescent, royal-purple hue, but when dry was blue-black in color. It was washed by decantation, first with water, then with concentrated ammonia, to extract the unchanged molybdic acid. The residue, blue-black in color and insoluble in ammonia, was dried at 100° and ignited to a dull red heat. It was found to lose weight, change to the white or light yellow of molybdic acid, and become easily soluble in ammonia. On igniting 0.5410 gram of the solid, 0.5148 gram resulted; according to the equation

$$2MoO_3.H_2O + O_2 = 2MoO_3 + 2H_2O,$$

there should result 0.5148 gram, therefore, the blue-black

[1] Ann. Chim. Phys., [5], 21, 199.

solid was hydrated molybdenum dioxide and the reaction of molybdic acid with dimethylarsine was :

$$2H_2MoO_4 + (CH_3)_2AsH = (CH_3)_2AsOOH + 2MoO_2.H_2O.$$

Lead Peroxide and Dimethylarsine.

When 0.66 gram of dimethylarsine (1 mol.), 15 grams of lead peroxide (1 mol.) and 50 cc. of water were brought into contact, in a sealed tube, a slow reaction was noticed ; the peroxide was gradually replaced by a metallic mirror and granular particles of lead, while the water was rendered opaque by a white, amorphous precipitate. After a number of days the tube was opened and its contents were found to fume and to give off an odor suggestive of cacodyl rather than that of unchanged arsine. The metallic particles were easily identified as lead ; the aqueous solution was proved to contain cacodylic acid. On standing, or treating with carbon dioxide, the aqueous solution was found to deposit a more voluminous precipitate,[1] therefore, lead cacodylate was in solution and the reactions of lead peroxide with dimethylarsine are as follows :

$$4(CH_3)_2AsH + 5PbO_2 = 2[(CH_3)_2AsOO]_2Pb + 3Pb + 2H_2O ;$$

$$4(CH_3)_2AsH + PbO_2 = 2[(CH_3)_2As]_2 + Pb + 2H_2O.$$

Anhydrous Ferric Chloride and Dimethylarsine.

When 3.1 grams of anhydrous ferric chloride (2 mols.) in ether solution, were treated, in a sealed tube, with 1.2 grams of dimethylarsine (excess 1 mol.) there resulted an immediate voluminous precipitate of ferrous chloride ; on being filtered from the ether solution and washed with ether, then with water, it gave Turnbull's blue with potassium ferricyanide, but no pink coloration with potassium thiocyanate. The ether solution had the odor of cacodyl chloride, which was

[1] Cacodylic acid dissolves lead peroxide or lead hydroxide but not metallic lead or lead carbonate. A neutral solution of lead hydroxide in cacodylic acid gives a white amorphous precipitate on being treated with carbon dioxide.

identified as such by treatment with hydrogen sulphide. The reaction was as follows :

$$(CH_3)_2AsH + 2FeCl_3 = (CH_3)_2AsCl + 2FeCl_2 + HCl.$$

Napoli concludes[1] that the action of ferric chloride on arsine is

$$3FeCl_3 + AsH_3 = 3FeCl_2.AsCl_3 + 3H.$$

Cacodyl Chloride and Dimethylarsine.

When molecular quantities of dimethylarsine and cacodyl chloride were mixed in a sealed tube and heated 2–3 hours, at 100°, an oil, less mobile than the original substances, was obtained. On cooling to —20° the oil crystallized in large, beautiful, white crystals ; it was identified as cacodyl by its melting point, its boiling point and its inflammability in air. As hydrochloric acid was detected on opening the tube, the following equation is justified :

$$(CH_3)_2AsH + (CH_3)_2AsCl = (CH_3)_2As.As(CH_3)_2 + HCl.$$

Platinic Chloride and Dimethylarsine.

A bulb containing 0.8 gram of dimethylarsine and 20 drops of a 10 per cent solution of platinic chloride were sealed in a tube filled with carbon dioxide. The capillary of the bulb was broken so that the arsine distilled slowly into the tube ; a brown-red precipitate was first formed, but it finally gave way to a bright yellow one. The tube was heated an hour, at 130° ; on cooling, complete solution of the precipitate and a heavy oil were noticed. On opening the tube an increase of 56.8 cc. of gas was observed ; after freeing from carbon dioxide and unchanged dimethylarsine, the residue, 28.8 cc., proved to be hydrogen.

Another tube, prepared as above and kept at the room temperature for a number of days, also yielded hydrogen, but the yellow solid remained largely undissolved.

After freeing the tube from the excess of dimethylarsine by exhausting with the pump, the contents, a heavy oil possessing fuming properties, proved to be cacodyl. After the latter was oxidized cacodyl chloride was detected by its odor and its precipitation with hydrogen sulphide.

[1] J. prakt. Chem., 64, 93.

When 0.59 gram of dimethylarsine (2 mols.) was treated with 4 cc. of a 10 per cent solution of platinic chloride (1 mol.) and the solution was evaporated nearly to dryness, light yellow, compact crystals were obtained. They were washed, dried and analyzed:

0.028 gram substance, dried at 110°, gave 0.0084 gram Pt.

Crystals from another sample were analyzed:

0.1048 gram substance gave 0.0348 gram Pt.

	Calculated for $[(CH_3)_2AsH]_2H_2PtCl_4$.	Found. I.	Found. II.
Pt	31.57	30.00	33.20

Evidently the substances formed were not homogeneous; this conclusion is confirmed by the following experiments:

When gaseous dimethylarsine was passed through a 10 per cent solution of platinic chloride, at ordinary temperatures, so that the latter was always present in excess, no hydrogen was formed, but a copious, dark brown precipitate. It was washed with water, alcohol and ether, then dried and analyzed:

0.0639 gram substance, dried in vacuum desiccator, gave 0.0248 gram Pt = 38.81 per cent.

0.0839 gram substance, dried at 78°, gave 0.0345 gram Pt = 41.12 per cent.

0.2362 gram substance, dried at 100°, gave 0.0990 gram Pt = 41.91 per cent.

0.0819 gram substance, dried at 110°, gave 0.0345 gram Pt = 42.12 per cent.

0.0854 gram substance, dried at 120°, gave 0.0360 gram Pt = 42.15 per cent.

0.1738 gram substance, dried at 130°, gave 0.0759 gram Pt = 43.65 per cent.

Theory for $(CH_3)_2AsHH_2PtCl_6$ = 38.10 per cent.

Theory for $(CH_3)_2AsClPtCl_4$ = 41.12 per cent.

Evidently, when platinic chloride is present in excess, 1 molecule of dimethylarsine unites with 1 molecule of platinic acid and, as seen above, when the dimethylarsine is present in excess, 2 molecules of it unite with 1 of platinic acid. The

formation of hydrogen and of $(CH_3)_2AsClPtCl_4$ can be expressed by the equation

$$(CH_3)_2AsH.H_2PtCl_6 = (CH_3)_2AsCl.PtCl_4 + H_2 + HCl.$$

However, the above data and studies are too limited to draw definite conclusions, either as to the composition of the various precipitates or as to their decompositions.

Bunsen describes[1] a platinic chloride salt of cacodyl chloride that agrees in composition with the formula

$$(CH_3)_2AsClPtO.H_2O.$$

He obtained a red-brown precipitate and recrystallized it from hot water, by which it was changed to colorless needles; we obtained the red-brown substance by his method and dried it in vacuum, when it gave the following results on analysis:

0.125 gram substance gave 0.0312 gram Pt = 24.96 per cent.

At 70° this red-brown substance gave off fumes of cacodyl chloride and changed to a lemon-yellow color. It was heated to constant weight and analyzed:

0.1240 gram substance gave 0.0487 gram Pt = 38.54 per cent, a value that agrees closely with Bunsen's (38.34) and with the theory of the substance he describes (38.48). Evidently this compound, like the platinic chloride salts of dimethylarsine, decomposes even by mild heating and, as was determined by experiment, varies largely in composition according to the method of preparation.

Soubeiran[2] and Simon[3] claimed that arsine precipitated metallic platinum from platinic chloride solutions; Napoli[4] gives the following equation:

$$3PtCl_4 + 2AsH_3 = 3Pt.2AsCl_3 + 6H,$$

while Tivoli[5] holds that the composition of the precipitate is HAsPtO. A closer study of the platinum and other salts of the arsines will be made during the year.

[1] Jahres. d. Chem., 21, 500.
[2] Ann. Chim. Phys., 43, 407.
[3] Pogg. Ann., 42, 563. Jahres. d. Chem., 1839, p. 138.
[4] J. prakt. Chem., 64, 93.
[5] Gazz. chim. ital., 14, 487. Jahres. d. Chem., 1884, p. 459.

Auric Chloride and Dimethylarsine.

When an excess of dimethylarsine (8 mols.) was treated, in a sealed tube, with an aqueous solution of gold chloride, an immediate precipitation and decolorization of the solution resulted. The first contact of the arsine with the solution gave rise to a light yellow, flocculent precipitate that was replaced, on mixing thoroughly, by a brown-black precipitate and a few golden flakes. The tube was opened and the excess of arsine was removed by heating on the water-bath and exhausting with the pump. The precipitate was washed with water, alcohol and ether and dried at 110°. Samples from two different experiments were analyzed :

0.0345 gram substance gave 0.0377 gram gold = 93.62 per cent.

0.0499 gram substance gave 0.0488 gram gold = 97.77 per cent.

The solution contained cacodyl, cacodyl chloride and cacodylic acid.

Napoli[1] considers the action of gold chloride on arsine to be as follows :

$$AuCl_3 + AsH_3 = Au.AsCl_3 + 3H.$$

Silver Nitrate and Dimethylarsine.

When gaseous dimethylarsine is treated with an excess of silver nitrate solution, the former is completely absorbed and the latter suffers a precipitation of a silver-like mirror or a gray-black, granular solid. When a mixture of dimethylarsine and an inert gas, such as hydrogen, is shaken with silver nitrate solution, it loses its arsine completely, as is shown by the loss of its fuming property when treated with air and also by the loss of its odor.

When 0.074 gram of dimethylarsine (1 mol.) was treated, in a sealed tube, with 1.2 grams of silver nitrate (1 mol.), dissolved in 24 cc. of water, an immediate reaction took place ; heat was evolved, the inner walls of the tube were coated with a silver mirror, and a large quantity of the black, granular

[1] J. prakt. Chem., 64, 93.

precipitate was formed. After washing with water, alcohol and ether, and drying at 95°,

0.4380 gram substance gave 0.5658 gram of AgCl = 97.29 per cent Ag.

Though largely composed of silver, in this case, evidently, other products are formed.

For the various opinions of the reactions of arsine with silver nitrate, consult Gmelin-Kraut's "Handbuch der Chemie."

Potassium Ferricyanide and Dimethylarsine.

When 0.93 gram of dimethylarsine (1 mol.) was treated with an aqueous solution of 10 grams of potassium ferricyanide (less than 4 mols.) and 2 grams of potassium hydroxide (less than 5 mols.), an immediate change of color to the yellow of potassium ferrocyanide resulted. In the reaction product potassium ferrocyanide, cacodyl and potassium cacodylate were identified. No potassium ferricyanide was found. Therefore, the reaction was quantitative according to the equations:

$$4K_3Fe(CN)_6 + 5KOH + (CH_3)_2AsH = 4K_4Fe(CN)_6 + (CH_3)_2AsOOK + 3H_2O;$$

$$4K_3Fe(CN)_6 + 4KOH + 4(CH_3)_2AsH = 2[(CH_3)_2As]_2 + 4H_2O + K_4Fe(CN)_6.$$

Parsons[1] concludes that none of the cyanic acids affect arsine.

Mercuric Chloride and Dimethylarsine.

When 1 molecule of mercuric chloride, in ether solution, was treated in a sealed tube, with a slight excess of 1 molecule of dimethylarsine, a flocculent, white precipitate was formed, but soon disappeared with the production of metallic mercury. On openihg the tube, the ether solution was evaporated; the residue contained no mercury and possessed the odor of cacodyl chloride, which was further identified by the hydrogen sulphide test. Therefore, the dimethylarsine reduced the mercuric chloride, quantitatively, to metallic mercury, according to the equation

[1] Chem. News, 35, 236.

$$(CH_3)_2AsH + HgCl_2 = (CH_3)_2AsCl + Hg + HCl,$$

with the probable intermediate reaction[1]

$$(CH_3)_2AsH + 2HgCl = (CH_3)_2AsCl + 2HgCl + HCl.$$

Sulphur and Dimethylarsine.

Sulphur reacts readily with dimethylarsine, forming different sulphides according to the quantity of sulphur used.

When 1.278 grams of dimethylarsine (2 mols.) were treated, in a sealed tube, with 0.8 gram of flowers of sulphur (excess 3 atoms) a gradual solution of the sulphur was noticed and the reaction was complete in 24 hours, at ordinary temperatures, the sulphur having changed to a white, crystalline solid. On opening the tube there was observed no arsine, but a pressure of hydrogen sulphide and a strong odor resembling asafœtida. The contents of the tube were extracted with hot alcohol, filtered, evaporated to dryness and the residue crystallized from ether. Small, granular crystals were obtained, having the characteristic odor of cacodyl sulphide. They melted at 50°, the melting point obtained by Bunsen[2] for cacodyl sulphide, $[(CH_3)_2As]_2S_2$:

$$2(CH_3)_2AsH + 3S = [(CH_3)_2As]_2S_2 + H_2S.$$

When sulphur is used in smaller proportions, liquid cacodyl sulphide[3] is formed. When 3.9 grams of dimethylarsine (2 mols.) were brought into contact with 1 gram of sulphur (less than 1 mol.), immediate reaction was shown by the evolution of heat; the solution was complete after standing 2–3 days. On opening the tube hydrogen sulphide, but no arsine, was given off. On distilling the liquid content of the tube it was found to boil mostly at 211°; the last fraction, boiling at 211°–220°, deposited crystals in the tube of the condenser; a residual red oil was identified as arsine trisulphide. The fraction boiling at 211° was analyzed:

0.1526 gram liquid gave 0.1428 gram $BaSO_4$.

[1] Cf. Primary Arsines. THIS JOURNAL, **33**, 127. For the reactions of arsine with mercuric chloride, *vide* Ann. Chim. Phys., **33**, 355. Pogg. Ann., **9**, 308; **81**, 423. Compt. rend., **79**, 118. Chem. News, **34**, 167. Jahres. d. Chem., **21**, 112.

[2] Ann. Chem. (Liebig), **46**, 16.

[3] *Ibid.*, **37**, 16.

	Calculated for $[(CH_3)_2As]_2S$.	Found.
S	13.22	13.15

On standing in contact with air, the oil formed a white, crystalline solid consisting of cacodylic acid and cacodyl disulphide. This is in accordance with the properties of cacody monosulphide as described by Bunsen.

Therefore, the reaction of dimethylarsine with a small quantity of sulphur, is as follows:

$$2(CH_3)AsH + 2S = [(CH_3)_2As]_2S + H_2S.$$

The above mentioned crystals, formed in the tube of the condenser, were pure white, glistening needles that were soluble in chloroform, carbon bisulphide and alcohol, but were insoluble in ether. They melted at 177°.5 and had a peculiar mercaptan-like odor.

	Calculated for $(CH_3)_2AsS$.	Found.
S	21.05	21.31

Their formation may be expressed by the equation:

$$6(CH_3)_2AsH + 10S = 4(CH_3)_2AsS + 3H_2S + As_2S_3.$$

The reactions of arsine with sulphur are reported to be as follows:[1]

$$2AsH_3 + 3S = 2As + 3H_2S;$$
$$2AsH_3 + 3S_2 = As_2S_3 + 3H_2S.$$

Sulphur Dioxide and Dimethylarsine.

When 2.17 grams of dimethylarsine (1 mol.) and 1.5 grams of liquid sulphur dioxide (excess of 1 mol.) were brought together in a sealed tube, immediate reaction took place; much heat was liberated and an orange-colored liquid was formed which, on standing, changed almost entirely to a white, crystalline solid. On opening the tube there was observed a slight pressure of a gas which contained no sulphur dioxide, hydrogen sulphide, or dimethylarsine, but which had the odor of asafœtida.

The small quantity of liquid was poured from the tube into

[1] Gmelin-Kraut: "Handbuch der Chemie."

a beaker, when it immediately began to deposit crystals which were found to melt at 50°, the melting-point of cacodyl disulphide. The crystalline solid in the tube was dissolved in hot alcohol and its solution evaporated to dryness on the water-bath; it gave a residue difficultly soluble in ether. The first ether extract gave white needles which melted at 165°–170°, $(CH_3)_3AsS$ melts at 170°. The second ether extract gave another crystalline solid which melted at 110°; CH_3AsS melts at that temperature.[1] The solid, left after extracting the ether, was found to contain cacodylic acid. Therefore, it is evident that cacodyl disulphide, methylarsine sulphide, trimethylarsine sulphide and cacodylic acid are products of the action of liquid sulphur dioxide on dimethylarsine. The reactions are represented by the equations:

$$7(CH_3)_2AsH + 4SO_2 = 2(CH_3)_2AsS + 2CH_3AsS + 3(CH_3)_2AsOOH + 2H_2O;$$

$$7(CH_3)_2AsH + 4SO_2 = 2[(CH_3)_2As]_2S_2 + 3(CH_3)_2AsOOH + 2H_2O.$$

Disulphur Dichloride and Dimethylarsine.

It was found by Michaelis and Luxenbourgh[2] that when disulphur dichloride acted upon dimethylamine, an oil, dithiodimethylamine, $[(CH_3)_2N]_2S_2$, was formed. It was expected that treatment of dimethylarsine with the same reagent would give dithiodimethylarsine or cacodyl disulphide; but it was found that the reaction proceeds further, disulphur dichloride acting as a chlorinating agent, formed cacodyl chloride and deposited free sulphur.

When 2 molecular proportions (1.9 grams) of dimethylarsine were mixed carefully with 1 of disulphur dichloride (1.2 grams) much heat was evolved and a yellow solid separated from the reaction-mixture. On opening the tube hydrogen sulphide was observed. The contents of the tube were extracted with ether and the ether solution was evaporated. The residue, smelling strongly of cacodyl chloride, was dissolved in water and identified by its immediate precipitation with hydrogen sulphide.

[1] Ann. Chem. (Liebig), 107, 269.
[2] Ber. d. chem. Ges., 28, 166.

The yellow solid, insoluble in ether, melted at 114°.5; rhombic sulphur melts at that temperature. Therefore, the above reaction was as follows:

$$2(CH_3)_2AsH + S_2Cl_2 = 2(CH_3)_2AsCl + S + H_2S.$$

Stannic Chloride and Dimethylarsine.

When stannic chloride reacts with dimethylarsine a reduction to metallic tin does not take place, but hydrochloric acid is eliminated and the compound ***dimethylarsine chlorstannide***, $(CH_3)_2As.SnCl_3$, is formed. This reaction is analogous to the formation of $(C_2H_5)_2N.SiCl_3$, $(C_2H_5)_2N.BCl_2$, etc., from dimethylamine.[1]

When 2 grams of dimethylarsine (1 mol.) and 4.9 grams of stannic chloride (1 mol.) were brought into contact, in a sealed tube, they reacted violently with a flame and the liberation of much heat, a white, crystalline solid being produced. When one end of the tube was heated at 100°, the solid sublimed to the cooler part, where it formed large, beautiful, colorless needles, some attaining the length of 2 cm. Dimethylarsine chlorstannide is quite stable in dry air, but is liquefied slowly by moist air. It has a very penetrating and disagreeable odor. It is easily soluble in ether and carbon bisulphide, but less so in chloroform.

I. 0.0314 gram substance required 0.0479 gram $AgNO_3$.
II. 0.1674 gram substance required 0.2559 gram $AgNO_3$.

	Calculated for $(CH_3)_2As.SnCl_3$.	Found. I.	II.
Cl	32.22	31.91	31.80

Phosphorus Trichloride and Dimethylarsine.

When phosphorus trichloride (5.5 grams) reacted, in a sealed tube, with 1 molecular proportion of dimethylarsine (5 grams) heat was evolved and an orange-yellow solid was precipitated.

On opening the tube a pressure of hydrochloric acid and an odor of cacodyl chloride were observed. The cacodyl chloride was identified by the boiling point (100°) and its immediate precipitation from a water solution by hydrogen sulphide.

[1] Ber. d. chem. Ges., 29, 710.

The orange solid was found to be insoluble in all ordinary organic solvents and to contain no arsenic. It was not obtained sufficiently pure for satisfactory analysis, but its high per cent of phosphorus makes it probable that it is $(CH_3P)_x$, or the compound $(CH_3)_2P_4$,[1] with which it agrees in properties.

Janowsky[2] found that arsine and phosphorus trichloride reacted as follows:

$$PCl_3 + AsH_3 = PAs + 3HCl.$$

Arsenic Trichloride and Dimethylarsine.

Four and a half grams of dimethylarsine (1 mol.) and 7.8 grams of arsenic trichloride (1 mol.) reacted at ordinary temperatures, liberating heat and forming an oil and a dark brown solid. The reaction products were extracted with chloroform and the chloroform solution, which smelled of cacodyl chloride, was distilled. After the chloroform had been removed the temperature rose to 100°–104°; the distillate was identified as cacodyl chloride. After washing with chloroform, alcohol and ether and drying at 110°, the brown, amorphous solid was analyzed:

0.4089 gram substance gave 0.7116 gram $Mg_2P_2O_7$.

	Calculated for $(CH_3As)_x$.	Found.
As	83.33	84.25

The substance was probably the polymer $(CH_3As)_x$ and some free arsenic. The equation representing the reaction is, perhaps,

$$2(CH_3)_2AsH + AsCl_3 = (CH_3)_2AsCl + (CH_3As)_x + 2HCl.$$

Janowsky[3] found that arsine and arsenic trichloride reacted as follows:

$$AsH_3 + AsCl_3 = 2As + 3HCl.$$

Antimony Trichloride and Dimethylarsine.

Dimethylarsine (3.8 grams) was brought into contact, in a sealed tube, with 1 molecular proportion of antimony trichlor-

[1] Ann. Chem. (Liebig), 104, 4.
[2] Ber. d. chem. Ges., 6, 216.
[3] *Ibid.*, 6, 219.

ide (8 grams); a heavy, transparent oil and a black, metallic deposit resulted. After heating 5 hours, at 100°, considerable pressure was observed; on opening the tube a gas (stibine), which gave an antimony mirror, was evolved. The black deposit was separated from the oil by means of ether and hydrochloric acid and identified as metallic antimony. Cacodyl chloride was easily recognized in the reaction products, by its odor and its precipitation as cacodyl sulphide. The heavy oil decomposed at ordinary temperatures, giving off a gas and depositing metallic antimony. It was probably an intermediate product of the action. The reactions, at least in part, are as follows:

$$3(CH_3)_2AsH + SbCl_3 = 3(CH_3)_2AsCl + SbH_3;$$
$$3(CH_3)_2AsH + 2SbCl_3 = 3(CH_3)_2AsCl + 2Sb + 3HCl.$$

Dibromsuccinic Acid and Dimethylarsine.

When dibromsuccinic acid (2 grams) was treated, in a sealed tube, with 1.5 grams of dimethylarsine (2 mols.) there was an immediate precipitation of a white, crystalline solid. No pressure was observed on opening the tube. After washing with ether and recrystallizing from water, the crystals melted at 185° and gave no test for bromine or arsenic. Therefore, they were succinic acid, which melts at 185°. Cacodyl bromide was identified in the ether solution. The reaction was

$$C_2H_2Br_2(COOH)_2 + 2(CH_3)_2AsH = C_2H_4(COOH)_2 + 2(CH_3)_2AsBr.$$

Aromatic Secondary Arsines.

These arsines, like the aliphatic secondary arsines, can be prepared by reducing the corresponding arsinic acids, no difference in the ease of their reductions being noticeable.

Diphenylarsinic acid, $(C_6H_5)_2AsOOH$, was chosen for reduction because of the ease with which it can now be prepared and purified. It was first obtained by Michaellis and La Coste[1] from diphenylarsine trichloride, the transformation being quantitative, according to the equation:

[1] Ann. Chem. (Liebig), 201, 231.

$$(C_6H_5)_2AsCl_3 + 2H_2O = (C_6H_5)_2AsOOH + 3HCl.$$

The trichloride is formed by chlorinating diphenylarsine chloride,

$$(C_6H_5)_2AsCl + Cl_2 = (C_6H_5)_2AsCl_3.$$

Having the monochloride, it is only necessary, therefore, to cover it with water, saturate with chlorine or bromine, and to warm, when complete transformation to the diphenylarsinic acid results, according to the two equations mentioned above. The only difficulty hitherto involved has been the preparation of pure diphenylarsine chloride. It has been produced, up to the present, by the application of Michaelis' general method for the formation of secondary aromatic compounds.[1]

The trialphylarsine is first obtained by condensing the alphyl monohalide and arsenic trichloride by means of sodium and is subsequently heated at 250°, in a sealed tube, with 4–5 parts of arsenic trichloride, for 30 hours.[2] The transformations are nearly quantitative, as follows:

$$3RCl + AsCl_3 + 6Na = R_3As + 6NaCl;$$
$$R_3As + 2AsCl_3 = 3RAsCl_2.$$

Monophenylarsine chloride thus obtained is then phenylated by heating to 255°, with less than 0.5 molecular quantity of mercury phenyl,[3] the reaction being, of course, far from quantitative, according to the equation:

$$C_6H_5AsCl_2 + (C_6H_5)_2Hg = (C_6H_5)_2AsCl + C_6H_5HgCl.$$

The mixture of mono- and diphenylarsine chlorides thus obtained is separable only by a laborious process of fractional distillation. By employing the following method, the preparation and use of mercury phenyl is dispensed with, a single process of dephenylation is substituted for both the dephenylation and the subsequent phenylation, and an admixture of diphenylarsine chloride with the mono- or the triphenyl arsenic compounds does not involve difficulties of separation.

[1] Ann. Chem. (Liebig), **201**, 215.
[2] Ber. d. chem. Ges., **27**, 263.
[3] Ann. Chem. (Liebig), **307**, 115.

Preparation of Diphenylarsinic Acid.

A mixture of 360 grams of triphenylarsine[1] (2 mols.) and 300 grams of arsenic trichloride (1 mol.) was heated at 220°, in sealed tubes, for 40 hours. The dark colored reaction product was then subjected to vacuum distillation, so as to separate arsenic trichloride, phenylarsine dichloride, diphenylarsine chloride, and triphenylarsine from one another as sharply as possible and to observe better the course of the dephenylation. For the preparation of phenylarsonic acid or diphenylarsinic acid from this mixture ordinary distillation will suffice, or it may be entirely dispensed with. The lowest fraction, boiling as high as 150° (23 mm.), was washed with a little water and extracted with ether, so as to free it from arsenic trichloride; on redistilling, 148 grams (19 per cent of the theory) of phenylarsine dichloride were obtained, boiling at 139° (23 mm.). The higher fractions yielded 163 grams (38 per cent of the theory) of diphenylarsine chloride, boiling at 210° (34 mm.).

It is impossible, or at least inconvenient and unnecessary, to obtain by distillation pure diphenylarsine chloride; the pure phenylcacodylic acid may be separated from adhering compounds by an application of the method of analysis (*c*) (*vide* p. 7).

For instance, suppose there are present in a mixture the following four substances—arsenic trichloride, phenylarsine dichloride, diphenylarsine chloride and triphenylarsine. On covering with water, treating with chlorine to the point of saturation, and then boiling, the following reactions take place:

$$AsCl_3 + 4H_2O + Cl_2 = H_3AsO_4 + 5HCl;$$

$$C_6H_5AsCl_2 + 3H_2O + Cl_2 = C_6H_5AsO_3H_2 + 4HCl;$$

$$(C_6H_5)_2AsCl + 2H_2O + Cl_2 = (C_6H_5)_2AsO_2H + 3HCl;$$

$$(C_6H_5)_3As + H_2O + Cl_2 = (C_6H_5)_3AsO + 2HCl.$$

The triphenyl arsenic compounds of the last equation are insoluble in water, therefore, after filtering, only the products of the first three reactions are in solution. On treating this

[1] Ann. Chem. (Liebig), 333, 62.

solution with magnesia mixture, in the cold, the arsenic acid is, of course, quantitatively precipitated; on treating this filtrate with an excess of magnesia mixture and boiling, the magnesium salt of phenylarsonic acid is precipitated; finally, on acidifying with hydrochloric acid, diphenylarsinic acid is almost quantitatively precipitated; 100 cc. of its saturated, aqueous solution, at 27°, contains only 0.028 gram of the acid.

In short, to prepare diphenylarsinic acid, heat to 220°, for 30 hours, a mixture of triphenylarsine and arsenic trichloride, in the proportions indicated by the equation

$$2(C_6H_5)_3As + AsCl_3 = 3(C_6H_5)_2AsCl.$$

When cool, pour into water and saturate with chlorine; filter and treat with an excess of magnesia mixture, boil and filter. On acidifying with hydrochloric acid, the diphenylarsinic acid separates first as an oil, then solidifies in beautiful, white needles. After recrystallizing once from water the acid was obtained pure. Analysis:

0.1646 gram substance gave 0.3234 gram CO_2 and 0.0602 gram H_2O.

	Calculated for $(C_6H_5)_2AsO_2H$.	Found.
C	54.96	54.78
H	4.20	4.06

The yield of the acid exceeded 40 per cent. Should it seem desirable, the phenylarsine dichloride may be separated as mentioned above and be converted into diphenylarsine chloride, the yield of diphenylarsinic acid may thus be raised to nearly 60 per cent; by the method of Michaelis[1] the yield did not exceed 18 per cent.

Since triphenylarsine and other trialphylarsines react with an excess of arsenic trichloride (8–10 mols.) to form the monoalphyl compounds[2] and, as shown above, 2 molecules of the tertiary arsine react, largely, with 1 molecule of arsenic trichloride so as to form the secondary compound; finally, as was shown in an experiment, triphenylarsine reacts with

[1] Ber. d. chem. Ges., 27, 264. Ann. Chem. (Liebig), 207, 115.
[2] Michaelis: Ann. Chem. (Liebig), 320, 272.

phenylarsine dichloride, when heated for 24 hours, at 240°, so as to form a large quantity of the secondary arsenic compound —it may be concluded that the proportions of the products formed at elevated temperatures depend largely upon mass influence. An effort to prepare diphenylarsine chloride by the application of this influence to the sodium condensation failed, the expected reaction :

$$2C_6H_5Cl + AsCl_3 + 4Na = (C_6H_5)_2AsCl + 4NaCl,$$

did not take place, only triphenylarsine being obtained. Benzyl chloride[1] and isoamyl chloride (*vide* p. 49), however, react, in the proportions of the above equation, giving large quantities of secondary arsine chlorides.

A discussion of the mechanism of these and other arsenic reactions will be given in a future paper.

Diphenylarsine.

This arsine, the analogue of diphenylamine, is prepared from diphenylarsinic acid :

$$(C_6H_5)_2AsOOH + 4H = (C_6H_5)_2AsH = 2H_2O.$$

in a manner nearly identical with that of the preparation of phenylarsine.[2] A quantity of the pure acid was mixed with an excess of amalgamated zinc dust and then covered with a layer of ether. The flask was connected with a reflux condenser, at the top of which was inserted a rubber stopper carrying a dropping funnel and a tube bent down into mercury ; the latter permits the exit of free hydrogen, but prevents the entrance of air.

Concentrated hydrochloric acid was placed in the dropping funnel and 5–20 cc. of it were admitted to the flask, occasionally, during 2 or 3 days, or until the completion of the reduction was assured.

During the reduction occasional energetic agitation of the flask is necessary, for two reasons : First, the arsine is soluble in ether but not in water (the diphenylarsinic acid is just the reverse) and, as it forms, it coats the zinc in contact with

[1] Ann. Chem. (Liebig), **233**, 62.
[2] Ber. d. chem. Ges., **34**, 3598. THIS JOURNAL, **33**, 147.

the lower aqueous layer, thus retarding the reduction process. Second, phenylcacodyl is an intermediate product of the reduction and it also coats the zinc and is dissolved, to some extent, by ether.[1] Therefore, energetic shaking, particularly at the end of the reduction, is necessary to extract the arsine and to cause complete reduction of the phenylcacodyl to diphenylarsine.

As the reduction progresses the hydrogen bubbles on the surface of the ether, become iridescent and a somewhat bluish tint is imparted to the ether solution. When the reduction is complete the solution is transferred, without contact with the air, to a separatory funnel containing some fused calcium chloride; then, after drying the ether solution, it is drawn over into a distilling flask connected with a condenser and a Brühl apparatus, which, previously, has been filled with carbon dioxide. When the apparatus is exhausted the ether may be removed and the distillation of the arsine effected. Usually so much frothing of the liquid takes place that difficulty is encountered in obtaining pure condensed vapor of the distilled substance; slow distillation, in a stream of pure carbon dioxide, gives the best results. The arsine thus obtained is a clear, colorless oil, that boils at 174° (25 mm.) and at 155° (37 mm.); from a consideration of the boiling points of its analogues and homologues,[2] diphenylarsine ought to boil at 250°–260°, under ordinary pressure.

In the dilute form its odor is not so pleasant as that of phenylarsine; its more concentrated vapor produces catarrhal symptoms and sneezing. It is soluble in alcohol, ether and other organic solvents, but is insoluble in water.

0.1500 gram liquid gave 0.3387 gram CO_2 and 0.0670 gram H_2O.

	Calculated for $(C_6H_5)_2AsH$.	Found.
C	62.61	61.58
H	4.78	4.96

Oxidation of Diphenylarsine.

In contact with air diphenylarsine warms and changes, al-

[1] Ber. d. chem. Ges., 18, 1955.

[2] This Journal, 33, 107.

most instantaneously, into a pure white or faintly yellow, hard mass; more rapid oxidation is easily discernible in the case of diphenylarsine than in that of phenylarsine. The mass was treated with excess of ammonia and warmed on the water-bath; partial solution took place. The insoluble portion was filtered, washed with water and recrystallized from ether; it was found to melt at 90° and, by its odor, was further identified as phenylcacodyl oxide.[1]

When acidified, the ammonia solution yielded crystals of diphenylarsinic acid, which was identified by its melting-point and other properties.[2] From 1.9 grams of the oxidation product, 1.7 grams of diphenylarsinic acid and 0.2 gram of cacodyl oxide were recovered, therefore about 88 per cent of the oxidation was represented by the first and 12 per cent by the second of the following equations:

$$(C_6H_5)_2AsH + O_2 = (C_6H_5)_2AsOOH,$$

$$2(C_6H_5)_2AsH + O_2 = [(C_6H_5)_2As]_2O + H_2O.$$

Slow oxidation is the favorable condition for the former reaction; an ether solution of the arsine, exposed to the air, precipitated only needles of diphenylarsinic acid.

Diphenylarsine and Bromine.

When 0.75 gram of diphenylarsine, in a sealed tube, was allowed to distil, slowly, into ether containing 1 gram of bromine (2 mols.) there was an immediate, voluminous precipitation of a reddish yellow solid; when the entire quantity of arsine had come into contact with the bromine, the color of the precipitate changed to a golden yellow and the crystals became compact and glistening; the ether solution was completely decolorized. On opening the tube the yellow, crystalline solid was removed, washed with ether and dried in a desiccator.

0.1656 gram substance required 0.1120 gram $AgNO_3$.

	Calculated for $(C_6H_5)_2AsBr_3$.	Found.
Br	51.17	49.82

[1] Ann. Chem. (Liebig), 201, 229.

[2] *Ibid.*, 201, 231.

Diphenylarsine tribromide forms golden yellow plates, which soften at 120° and melt at 129°. It attacks the skin with great avidity. Water decomposes it, forming a light yellow oil, phenylcacodyl bromide. The equation for the formation of the tribromide is as follows:

$$(C_6H_5)_2AsH + 2Br_2 = (C_6H_5)_2AsBr_3 + HBr.$$

Diphenylarsine and Iodine.

When 0.9 gram of diphenylarsine (1 mol.) was treated, in a sealed tube, with 1.94 grams of iodine (less than 2 mols.) in ether solution, there resulted an immediate precipitation of a dark red oil. On opening the tube a pressure of hydriodic acid was observed. From the reaction products an oil was isolated whose analysis agreed closely with the compound, *diphenylarsine iodide.*

0.2185 gram substance gave 0.1417 gram AgI.

		Calculated for $(C_6H_5)_2AsI$.
I	35.67	35.07

Under the above conditions diphenylarsine reacted with iodine according to the equation

$$(C_6H_5)_2AsH + I_2 = (C_6H_5)_2AsI + HI.$$

Diisoamylarsine Compounds.

There has, hitherto, been no easy, general method for the preparation of aliphatic secondary arsenic compounds. The dry distillation of the alkali salts of fatty acids with arsenic trioxide has yielded, as yet, only secondary methyl compounds. The treatment of alkyl iodides with sodium arsenide[1] has produced secondary ethyl compounds, but no general application has been made of this reaction, largely on account of the disagreeable properties of the sodium arsenide and because its reaction with alkyl halides gives rise to mixtures of the primary, secondary and tertiary arsine derivatives which, hitherto, have been difficult to separate.

Michaelis and Paetow[2] found that when 2 molecular proportions of benzyl chloride were condensed, by means of sodium,

[1] Ann. Chem. (Liebig), **89**, 319.
[2] *Ibid.*, **233**, 62.

with 1 molecular proportion of arsenic trichloride, the secondary arsine compound was formed in the largest quantity, according to the equation

$$2C_6H_5CH_2Cl + AsCl_3 + 4Na = (C_6H_5CH_2)_2AsCl + 4NaCl.$$

We have found that this reaction is applicable to the aliphatic series, for, when varied alkyl halides, such as ethyl bromide, propyl iodide and isoamyl chloride were treated in a similar manner, and their products were subjected to the same method of separation as the phenyl compounds (*vide* p. 43), solutions containing secondary arsine compounds were obtained.

In the case of isoamyl chloride, the main product was ***diisoamyl chloride*** or its basic compound, similar in composition to the basic cacodyl chloride obtained by Bunsen[1] and having the general formula, $6R_2AsCl.(R_2As)_2O$.

A quantity of liquid was obtained boiling at a temperature lower than that of diisoamylarsine chloride; it has not yet been isolated and identified, but it is probably isoamylarsine chloride, $C_5H_{11}AsCl_2$. Therefore, when alkyl halides, in general, are condensed with arsenic trichloride, by means of sodium, the mono- and dialkylarsine chlorides are formed and their relative proportions are governed by the molecular quantities of the alkyl halides and arsenic trichloride used. The general reactions are represented thus:

$$RCl + AsCl_3 + 2Na = RAsCl_2 + 2NaCl;$$
$$2RCl + AsCl_3 + 4Na = R_2AsCl + 4NaCl.$$

Diisoamylarsine Chloride.

In a 1 liter, round-bottomed flask, connected with a reflux condenser, were placed 62 grams of sodium wire (4 atoms) and 400–500 cc. of dry ether. Through a cork at the top of the condenser were inserted a dropping funnel and a glass tube, bent down into mercury, so as to prevent the entrance of air. After filling the apparatus with carbon dioxide, a mixture of 145 grams of isoamyl chloride (2 mols.) and 124 grams of arsenic trichloride (1 mol.) was added to the sodium, in small quantities at a time. The reaction was very energetic; a small por-

[1] Ann. Chem. (Liebig), 37, 49.

tion of the mixture (5 cc.) caused very violent boiling of the ether, consequently it was necessary to cool the flask by means of water. The isoamyl chloride and arsenic trichloride were added slowly, until the end of the operation; small portions, even at the end, caused quite a vigorous action. The reaction was complete in 2 hours. The ether solution was then filtered from the residue of sodium chloride and the latter was extracted several times with ether. After distilling off the ether there remained a colorless oil, which was fractionated *in vacuo*, with the following results:

Fraction.	Temperature.	Pressure. mm.	Weight. Grams.
1	140°	43	15
2	140°–148°	40–33	34
3	148°–152°	33–27	34
4	152°–160°	27–28	30
			115

Theory, $(C_5H_{11})_2AsCl = 172$

After one refractionation *in vacuo* and several under ordinary pressure, most of the liquid was found to boil at 263° (750 mm.). The distillation-product was a colorless oil containing, invariably, a little white, soapy precipitate.

0.1710 gram clear liquid gave 0.3036 gram CO_2 and 0.1478 gram H_2O.

	Calculated for $6(C_5H_{11})_2AsCl.[(C_5H_{11})_2As]_2O$.	Found.
C	48.65	48.94
H	8.96	9.60

Basic isoamylcacodyl chloride is a colorless liquid, boiling at 263° (750 mm.) and at 148° (33 mm.). It has a peculiar and characteristic odor, not at all intense like that of cacodyl chloride. It is soluble in all the ordinary organic media, but is insoluble in water. The white, soapy solid which always separates on distilling the oil is probably *isoamylcacodylic oxide*, $[(C_5H_{11})_2As]_2O$.

In this application of the Würtz reaction to aliphatic arsenic compounds a red, amorphous solid is always formed; it is larger in quantity when the reaction is conducted in the pres-

ence of air than in its absence. In the above condensation 20 grams of this red product were obtained, while in another experiment, during which air was freely admitted, 44 grams of it were formed. The red body was decolorized by means of bromine water and yielded a yellow, crystalline solid, which was easily soluble in ammonia. From the ammoniacal solution arsenious acid, isoamylarsonic acid, and isoamylarsinic acid were obtained, in about equal quantities. The red substance is probably similar to Bunsen's "erytrarsine," $(RAs)_4As_2O_3$, which would account for the isoamylarsonic acid and the arsenious acid formed by the above treatment, while an analogous dialkyl compound, $[(C_5H_{11})_2As]_4.As_2O_3$, would account for the formation of the isoamylarsinic acid.

Diisoamylarsine Chlordibromide.

A dry, ethereal solution of diisoamylarsine chloride was treated with bromine, in ether solution, until no decolorization resulted on warming gently. The ether was evaporated and the residual oil was permitted to stand; well formed, crystalline granules separated after some time, but only to the extent of about one-third of the oil. They were filtered, washed with benzene and analyzed:

0.1412 gram substance gave 0.1868 gram AgCl.2AgBr, which is equal to 0.1351 gram AgBr.

	Calculated for $(C_5H_{11})_2AsCl.Br_2$.	Found.
Br	41.61	41.47

Diisoamylarsine chlordibromide is a pure white, crystalline solid which melts at 124°–125° and has an odor resembling that of chloral hydrate. It is readily soluble in ether and chloroform, but is less so in benzene. Water dissolves it slowly, ammonia very readily, with the formation of *isoamylarsinic acid.*

The equation representing the formation of the above trihalide is as follows:

$$(C_5H_{11})_2AsCl + Br_2 = (C_5H_{11})_2AsCl.Br_2.$$

The incompleteness of this reaction is probably due to the following ones :[1]

$$(C_5H_{11})_2AsCl.Br_2 = C_5H_{11}AsBr_2 + C_5H_{11}Cl,$$

or $$(C_5H_{11})_2AsCl.Br_2 = C_5H_{11}AsClBr + C_5H_{11}Br.$$

The decomposition products, being liquids and being formed to a large extent, account for the small yield of the pentavalent arsenic derivative.

Diisoamylarsine Sulphide, $[(C_5H_{11})_2As]_2S$.

When diisoamylarsine chloride is added to water and is treated with hydrogen sulphide, beautiful white needles separate at the surface of the water. When the reaction was complete, after 10 hours, the crystals were extracted with ether; the latter having been removed, an oil remained. It solidified in a freezing mixture and yielded crystals. Analysis :

0.1751 gram substance gave 0.0890 gram $BaSO_4$.

	Calculated for $[(C_5H_{11})_2As]_2S$.	Found.
S	6.86	6.98

The sulphide melts at 29°–30°, is easily soluble in ether and carbon bisulphide, difficultly soluble in alcohol and insoluble in water. The equation for its formation is as follows :

$$2(C_5H_{11})_2AsCl + H_2S = [(C_5H_{11})_2As]_2S + 2HCl.$$

Isoamylarsinic Acid.

Isoamylarsinic acid was prepared from isoamylcacodyl chloride, by a method similar to that used for the preparation of phenylarsinic acid from phenylcacodyl chloride. Isoamylcacodyl chloride was covered with water, treated with bromine and heated until the excess of bromine was decolorized; the treatment was repeated until the bromine was no longer absorbed. By this means the oil was changed to a yellow, crystalline solid, which was found to be soluble in ammonium hydroxide. To the ammoniacal solution an excess of magnesium chloride was added in the cold, to precipitate arsenious acid; then the precipitate was boiled to precipitate the magnesium salt of isoamylarsonic acid, formed from isoamylarsine chloride

[1] Cf. Ethylcacodyl Iodide. Ann. Chem. (Liebig), 116, 367.

and which had not been completely removed by distillation. After filtering off the magnesium salt of the arsonic acid, the solution was made slightly acid, when the *isoamylarsinic acid* was precipitated as large, flaky crystals. After recrystallizing from water it was obtained pure.

I. 0.1132 gram substace gave 0.1175 gram CO_2 and 0.0970 gram H_2O.

II. 0.2620 gram substance gave 0.4030 gram CO_2 (H_2O was lost).

	Calculated for $(C_5H_{11})_2AsOOH.2H_2O$.	Found. I.	Found. II.
C	41.95	41.67	41.95
H	9.69	9.27	. .

Isoamylarsinic acid melts at 153°-154°. It is easily soluble in alcohol, somewhat so in water and insoluble in ether. The equation of its formation is as follows:

$$(C_5H_{11})_2AsCl + Br_2 + 2H_2O = (C_5H_{11})_2AsOOH + HCl + 2HBr.$$

Diisoamylarsine.

This arsine was prepared by the method employed for diphenylarsine, 26 grams of pure diisoamylarsinic acid being used and yielding nearly the theoretical quantity of diisoamylarsine. No difficulty was encountered in distilling the arsine, a pure product being obtained at 150° (99 mm.).

0.1347 gram substance gave 0.2715 gram CO_2 and 0.1238 gram H_2O.

	Calculated for $(C_5H_{11})_2AsH$.	Found.
C	55.05	54.97
H	10.09	10.21

The physical properties of diisoamylarsine are quite like those of diphenylarsine; however, it has a sickening, characteristic odor, more suggestive of isoamyl alcohol than of arsine.

Oxidation Products.

On exposing diisoamylarsine to the air a more syrupy product was obtained than from diphenylarsine. On passing air

into a beaker containing 1 gram of diisoamylarsine, sufficient heat was evolved to boil some of the arsine, but no flame reaction was produced. The oxidation products were extracted, first with ammonia, then with ether. The former extract yielded diisoamylarsinic acid and the latter an oil, which was probably diisoamylcacodylic oxide.

The preparation and study of arsines, stibines and phosphines by reactions described in the preceding pages are being pursued in this laboratory.

URBANA, ILL.,
July 14, 1905.

Contributions from the Sheffield Laboratory of Yale University.

CXXVIII.—SOME DERIVATIVES OF BENZENESULPHONYLAMINOACETONITRILE.

BY TREAT B. JOHNSON AND ELMER V. MCCOLLUM.

In the course of some work on the preparation of derivatives of adrenaline we had occasion to prepare benzenesulphonesarcosine. We find that this acid can easily be prepared from benzenesulphonylaminoacetonitrile.[1] When this compound was treated with methyl iodide, in presence of sodium ethylate, it was converted into benzenesulphonylmethylaminoacetonitrile (I.). This nitrile was easily hydrolyzed by hydrochloric or sulphuric acid to benzenesulphonylsarcosine (II.).

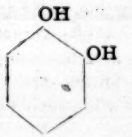
$$C_6H_5SO_2NHCH_2CN + CH_3I + C_2H_5ONa = C_6H_5SO_2N(CH_3)CH_2CN + NaI + C_2H_5OH.$$
I.

$$C_6H_5SO_2N(CH_3)CH_2CN + 2H_2O = C_6H_5SO_2N(CH_3)CH_2COOH + NH_3.$$
II.

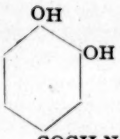
It seemed of interest to examine the behavior of this acid (II.) towards pyrocatechol. It might be expected to condense with pyrocatechol,[2] in presence of zinc chloride or phosphorus oxychloride, to give a benzenesulphonylmethylaminoacetopyrocatechol (III.):

[1] Knovenagel and Lebach: Ber. d. chem. Ges., 37, 4094.

[2] Dzersgowski: Jour. der russ. chem. Ges., 35, 154. Bruhns: Ber. d. chem. Ges., 34, 92.



$$+ C_6H_5SO_2N(CH_3)CH_2COOH =$$

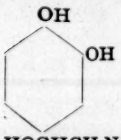


$$+ H_2O.$$

$$COCH_2N(CH_3)SO_2C_6H_5$$

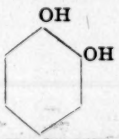
III.

Such a condensation would be of special interest since, on reduction, the ketone should give a benzenesulphone derivative of adrenaline[1] (IV.) if the structure of adrenaline is to be represented as in Formula V. :[2]



$$HOCHCH_2N(CH_3)SO_2C_6H_5$$

IV.



$$HOCHCH_2NHCH_3$$

V.

We now find that benzenesulphonesarcosine (II.) does not condense with pyrocatechol under the conditions which we employed. When we used either zinc chloride or phosphorus oxychloride as the condensing agent the only definite product isolated was unaltered acid. The same result was obtained when we attempted to condense benzenesulphonylaminoacetic acid with pyrocatechol. The acid, melting at 166°, was recovered unaltered.

[1] Fürth: Monatsh. Chem., **24**, 278 (1903).

[2] Jowett: P. Chem. Soc., **20**, 18 (1904). Friedman: Beitr. chem. Phys. Pathol., **6**, 92 (1904). Stolz: Ber. d. chem. Ges., **37**, 4149 (1904).

In the course of our work we have prepared a series of nitriles analogous to benzenesulphonylmethylaminoacetonitrile (I.). With the exception of the ethyl and propyl derivatives they have all proved to be well crystallized compounds. In every case that we have examined they have undergone hydrolysis to the corresponding acids when warmed with hydrochloric or sulphuric acid. In the case of the lower aliphatic derivatives the hydrolysis could be effected on the steam-bath, while with the higher aromatic derivatives it was necessary to heat in sealed tubes at a high temperature.

When benzenesulphonylaminoacetonitrile was treated with ethyl chloracetate, in the presence of sodium ethylate, it was converted, practically quantitatively, into ethyl benzenesulphonylcyanmethylaminoacetate (VI.):

$$C_6H_5SO_2NHCH_2CN + ClCH_2COOC_2H_5 + NaOC_2H_5 = C_6H_5SO_2N(CH_2CN)CH_2COOC_2H_5 + NaCl + C_2H_5OH.$$

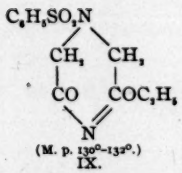
VI.

Especially interesting was the behavior of this ethyl ester (VI.) when saponified with dilute sodium hydroxide. The resulting benzenesulphonylcyanmethylacetic acid (VII.) immediately underwent a rearrangement in the alkaline solution, to an isomeric piperazine derivative (VIII.). That we were dealing here with a molecular rearrangement was established by the following experiment: When the silver salt of the product obtained by saponification (VIII.) was treated with ethyl iodide, an ethyl derivative (IX.) was obtained, which was not identical with the original ester (VI.).

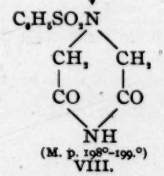
$C_6H_5SO_2N(CH_2CN)CH_2COOC_2H_5$ ⟶

(M. p. 68°–70°.)
VI.

$C_6H_5SO_2N(CH_2CN)CH_2COOH$
(Not isolated.)
VII.



(M. p. 130°–132°.)
IX.

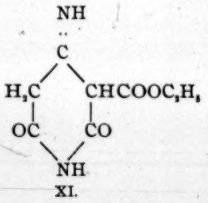


(M. p. 198°–199.°)
VIII.

This rearrangement is analogous to that of orthocyanbenzoic acid into phthalimide.[1] Two similar rearrangements have also recently been described by Thorpe[2] and his co-workers. They have shown that monoethyl α-cyan-β-iminoglutarate (X.) readily rearranges to α,α'-diketo-β-carbethoxy-γ-iminopiperidine (XI.) in the presence of strong sulphuric acid :

$$NCCH(COOC_2H_5)C : NHCH_2COOH \rightarrow$$

X.

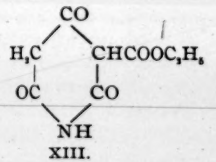


XI.

γ-Carbethoxy-γ-cyanacetoacetic acid (XII.) also underwent a similar change, when heated above its melting-point, and was transformed into 2,4,6-trioxy-3-carbethoxypyridine (XIII.) :

$$NCCH(COOC_2H_5)COCH_2COOH \rightarrow$$

XII.



XIII.

Hedin[3] observed that benzenesulphonylaminoacetic acid could be boiled with hydrochloric or sulphuric acid without decomposition. We now find that the nitrogen substituted benzenesulphonylaminoacetic acids are extremely stable and can be decomposed only by very energetic hydrolysis. When benzenesulphonylmethylaminoacetic acid (II.) was boiled with

[1] Hoogewerf and Van Dorp: Rec. Trav. Chim., **11**, 93.
[2] Baron, Remfrey and Thorpe: J. Chem. Soc., **85**, 1730 (1904).
[3] Ber. d. chem. Ges., **23**, 3196.

strong hydrochloric acid it was converted into the benzenesulphonic acid salt of sarcosine (XIV.):

$$\underset{\text{II.}}{C_6H_5SO_2N(CH_3)CH_2COOH} + H_2O = \underset{\text{XIV.}}{C_6H_5SO_2OHNH(CH_3)CH_2COOH}$$

This result is perfectly analogous to a previous observation by Schotten and Schlörmann.[1] They have shown that benzenesulphonylaminovalerianic acid (XV.) is hydrolyzed to the sulphonic acid salt of aminovalerianic acid (XVI.) when heated with hydrochloric acid at 180°:

$$\underset{\text{XV.}}{C_6H_5SO_2NH(CH_2)_4COOH} + H_2O = \underset{\text{XVI.}}{C_6H_5SO_2OHH_2N(CH_2)_4COOH}.$$

E. Fischer[2] has shown that hippuric acid is converted into hippuryl chloride when it is dissolved in acetyl chloride and then carefully treated with phosphorus pentachloride. It seemed of interest to examine the behavior of benzenesulphonylaminoacetic acid under the same conditions. We now find that this acid reacts in an entirely different manner with phosphorus pentachloride. The benzenesulphonyl radical was removed by this treatment with the formation of benzenesulphone chloride. The acid chloride was identified by means of its anilide, which melted sharply at 110°. This remarkable result is especially interesting in view of the stability of the benzenesulphonylaminoacetic acids when warmed with hydrochloric acid.

EXPERIMENTAL PART.

Benzenesulphonylaminoacetonitrile, $C_6H_5SO_2NHCH_2CN$.—This nitrile has previously been prepared by Knovenagel and Lebach.[3] They obtained it by treating benzenesulphonylamide with potassium cyanide and a sodium bisulphite solution of formaldehyde. We have prepared the nitrile by treating aminoacetonitrile[4] with benzenesulphonyl chloride.

[1] Ber. d. chem. Ges., 24, 3692.
[2] *Ibid.*, 38, 612.
[3] *Loc. cit.*
[4] Klages: Ber. d. chem. Ges., 36, 1514.

The sulphuric acid salt of aminoacetonitrile was dissolved in water and a layer of benzene poured over the surface of the solution. Benzenesulphonyl chloride and sodium hydroxide solution were then added alternately, in small portions. After the final addition of benzenesulphonyl chloride, the solution was made slightly alkaline and allowed to stand at the ordinary temperature, with occasional shaking. In the course of a few hours the nitrile separated in the layer of benzene as a beautiful, crystalline solid; this was filtered off and purified by crystallizing from benzene. It was insoluble in cold water. It separated from hot water as an oil, which solidified, on cooling, in the form of needles. It melted sharply at 80° with no effervescence. This melting point is somewhat higher than that given by Knovenagel and Lebach.[1] They state that their product melted at 76°–77°. Analysis:

	Calculated for $C_8H_8O_2N_2S$.	Found. I.	II.	III.
N	14.28	14.5	14.06	14.24

Benzenesulphonylmethylaminoacetonitrile, $C_6H_5SO_2N(CH_3)CH_2CN$.—This nitrile was first prepared by allowing methyl iodide to act on the silver salt of benzenesulphonylaminoacetonitrile. It can be obtained more easily by dissolving the nitrile in alcohol containing the calculated amount of sodium ethylate and warming with a molecular proportion of methyl iodide. The reaction is very smooth and the solution is neutral to litmus in a few minutes. After evaporating the alcohol and treating the residue with cold water, to remove sodium iodide, the nitrile remained as a crystalline product. It was deposited from water in beautiful plates and melted, to a clear oil, at 97°. Analysis:

	Calculated for $C_9H_{10}O_2N_2S$.	Found. I.	II.
N	13.33	13.70	13.40

Benzenesulphonylmethylaminoacetic Acid, $C_6H_5SO_2N(CH_3)CH_2COOH$.—This acid was obtained when benzenesulphonylmethylaminoacetonitrile was digested on the steam-bath with concentrated hydrochloric acid. The saponification is very smooth and the acid separates from the

[1] *Loc. cit.*

warm solution as a colorless, crystalline deposit. It crystallized from hot water in prisms and melted, to a clear oil, at 179°. It was very soluble in alcohol. Analysis:

	Calculated for $C_9H_{11}O_4NS$.	Found.
N	6.11	6.48

Ethyl Benzenesulphonylmethylaminoacetate, $C_6H_5SO_2N(CH_3)CH_2COOC_2H_5$.—This compound was prepared by esterifying the above acid with alcohol and sulphuric acid. It was obtained as an oil, which showed no signs of solidifying in a freezing mixture. It distilled at 215°–216° (15 mm.). Analysis:

	Calculated for $C_{11}H_{15}O_4NS$.	Found.
N	5.44	5.29

Behavior of Benzenesulphonylmethylaminoacetic Acid on Hydrolysis.—Eight grams of the acid were boiled with hydrochloric acid for 15 hours. When the acid solution was evaporated to dryness we obtained a semi-solid residue which was somewhat colored. This was dissolved in water and the solution boiled after adding some mercuric oxide. The color was entirely removed by this treatment and a yellow precipitate formed, which was separated by filtration. The filtrate was then saturated with hydrogen sulphide to remove dissolved mercury. After filtering from mercuric sulphide the aqueous solution was evaporated to dryness. We obtained a thick oil, which was extremely soluble in water. On long standing it finally solidified. It separated from its concentrated, aqueous solution in prisms and melted sharply at 136°–137°. A nitrogen determination agreed with the calculated for the benzenesulphonic acid salt of sarcosine.

	Calculated for $C_9H_{13}O_5NS$.	Found.
N	5.66	5.74

Two and one-half grams of benzenesulphonylmethylaminoacetic acid were heated with concentrated, aqueous ammonia, for 2 hours, at 150°–155°. When the ammoniacal solution was evaporated to dryness and the residue acidified with sulphuric

acid the unaltered acid was obtained. The acid was again recovered unaltered after heating with concentrated ammonia, at 180°–190°, for 2 hours.

Benzenesulphonylethylaminoacetonitrile,
$C_6H_5SO_2N(C_2H_5)CH_2CN$.—This nitrile was obtained as an oil which showed no signs of solidifying after standing for 2 weeks. When an attempt was made to purify it by distillation under diminished pressure it slowly decomposed, the chief portion boiling at 225°–235° (21 mm.). This crude nitrile was used for preparing the acid.

Benzenesulphonylethylaminoacetic Acid,
$C_6H_5SO_2N(C_2H_5)CH_2COOH$.—The acid was easily prepared by successively evaporating the above nitrile with concentrated hydrochloric acid. It crystallized from water in colorless plates, melting at 116°. Analysis:

0.8218 gram substance gave 0.8059 gram $BaSO_4$ (Carius).

	Calculated for $C_{10}H_{13}O_4NS$.	Found.
S	13.16	13.46

Benzenesulphonyl-n-propylaminoacetonitrile,
$C_6H_5SO_2N(C_3H_7)CH_2CN$.—This nitrile was obtained as an oil which refused to solidify after standing for over a month. No attempt was made to distil the nitrile and the crude material was converted into the acid.

Benzenesulphonyl-n-propylaminoacetic Acid,
$C_6H_5SO_2N(C_3H_7)CH_2COOH$.—This acid was obtained by hydrolyzing the above nitrile with concentrated hydrochloric acid. It was purified by repeated recrystallizations from hot water. It separated from its aqueous solution first as an oil, which finally solidified in the form of stout prisms, which melted at 99°–101° to a clear oil. It was very soluble in the ordinary organic solvents. Analysis:

	Calculated for $C_{11}H_{15}O_4NS$.	Found.
N	5.44	5.85

Benzenesulphonylcarbethoxyaminoacetonitrile,
$C_6H_5SO_2N(COOC_2H_5)CH_2CN$.—The potassium salt of benzenesulphonylaminoacetonitrile, which was prepared according to

Knoevenagel and Lebach's[1] directions, was suspended in benzene and a molecular proportion of ethyl chlorformate added. The solution was then heated on the steam-bath for 10–12 hours, when the reaction was complete. The benzene was evaporated on the steam-bath and the nitrile washed with cold water to remove potassium chloride. The nitrile was insoluble in water. It crystallized from alcohol in the form of sheaves of needles and melted at 83°–85°, without effervescence, to an oil. Analysis:

	Calculated for $C_{11}H_{12}O_4N_2S$.	Found.
N	10.44	10.48

When this nitrile was heated to 50°–60°, with 20 per cent sodium hydroxide solution it dissolved to a clear liquid. Upon acidifying this alkaline solution with hydrochloric or sulphuric acid carbon dioxide was evolved, and an immediate precipitate was obtained. It was identified as unaltered *benzenesulphonylaminoacetonitrile*, melting at 80°. Analysis:

	Calculated for $C_8H_8O_2N_2S$.	Found.
N	14.33	14.55

Benzenesulphonylbenzylaminoacetonitrile, $C_6H_5SO_2N(CH_2C_6H_5)CH_2CN$.—This nitrile was prepared in the usual way, by acting on the sodium salt of benzenesulphonylaminoacetonitrile with benzyl chloride. It was very soluble in benzene and alcohol, but insoluble in water. It crystallized from dilute alcohol in colorless prisms, melting at 68°–70°. Analysis:

	Calculated for $C_{15}H_{14}O_2N_2S$.	Found.
N	9.79	9.83

Benzenesulphonylbenzylaminoacetic Acid, $C_6H_5SO_2N(CH_2C_6H_5)CH_2COOH$.—This acid was obtained by prolonged hydrolysis of its nitrile with concentrated hydrochloric acid. It was insoluble in both hot and cold water. It was extremely soluble in alcohol and glacial acetic acid. When the latter solution was diluted with water the acid

[1] *Loc. cit.*

separated first as an oil, which soon solidified in the form of needles. It melted at 123°–125°. Analysis:

	Calculated for $C_{18}H_{18}O_4NS$.	Found.
N	4.59	4.79

Benzenesulphonyl-p-nitrobenzylaminoacetonitrile, $C_6H_5SO_2N(CH_2C_6H_4NO_2)CH_2CN$. — From benzenesulphonylaminoacetonitrile and paranitrobenzyl chloride. It was readily soluble in hot alcohol and separated, on cooling, in the form of prisms. It melted at 123°–125°. Analysis:

	Calculated for $C_{18}H_{17}O_4N_3S$.	Found.
N	12.68	12.80

Benzenesulphonyl-p-nitrobenzylaminoacetic Acid, $C_6H_5SO_2N(CH_2C_6H_4NO_2)CH_2COOH$. —This acid could not be obtained under the same conditions as the preceding acids described in this paper. In order to hydrolyze the corresponding nitrile it was necessary to heat with concentrated hydrochloric acid at 145°–150°, for 5 hours. It crystallized from alcohol in hair-like needles and melted, with decomposition, at 210°–212°. Analysis:

	Calculated for $C_{18}H_{18}O_6N_2S$.	Found.
N	8.00	7.61

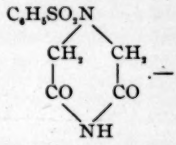
An attempt was made to hydrolyze this acid to paranitrobenzylaminoacetic acid, by heating with hydrochloric acid. After heating for 6 hours, at 170°–180°, the acid was recovered unaltered and melting sharply at 210°–212°, with effervescence. It was again heated for 3 hours, at 200°. Under these conditions the acid was completely decomposed into resinous material.

Ethyl benzenesulphonylcyanmethylaminoacetate, $C_6H_5SO_2N(CH_2CN)CH_2COOC_2H_5$. — Benzenesulphonylaminoacetonitrile was dissolved in alcohol containing a molecular proportion of sodium ethylate. To this solution was added the calculated quantity of ethyl chloracetate and it was then heated on the steam-bath until the solution was neutral to litmus. After evaporating the alcohol and treating as usual with water,

an oil, was obtained which finally solidified. It was washed with a cold, dilute solution of sodium hydroxide and then crystallized from benzene and petroleum ether. It crystallized in radiating needles, which melted at 68°–70°. Analysis:

	Calculated for $C_{12}H_{14}O_4N_2S$.	Found.
N	9.92	9.55

2,6-Diketo-4-benzenesulphonylpiperazine,



This piperazine derivative was obtained when the above ethyl benzenesulphonylcyanmethylaminoacetate was warmed with sodium hydroxide solution, at 53°, until all had dissolved. When the alkaline solution was acidified with hydrochloric or sulphuric acid the piperazine separated in the form of prisms. It melted at 198°–199°, with violent effervescence. Analysis (Kjeldahl):

	Calculated for $C_{10}H_{10}O_4N_2S$.	Found.
N	11.02	11.17

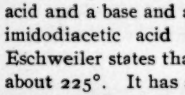
This compound was very stable in contact with concentrated sulphuric acid. It was dissolved in concentrated sulphuric acid and allowed to stand for 3 hours. When water was added to the acid solution the unaltered piperazine separated and melted sharply at 198°–199°. The compound is soluble in sodium hydroxide. Addition of silver nitrate produces a white, crystalline precipitate of the silver salt.

Behavior of 2,6-diketo-4-benzenesulphonepiperazine towards Hydrochloric Acid.—Three and three-tenths grams of the piperazine were heated in a sealed tube, with concentrated hydrochloric acid, for 2 hours, at 140°–150°. On cooling, long, needle-like prisms separated. The hydrochloric acid was evaporated on the steam-bath and the crystalline residue was recrystallized from alcohol. It separated in stout prisms which decomposed, with effervescence, at 225°–240°. The

crystals were free from sulphur but contained chlorine. The compound was extremely soluble in water. It behaved in every respect like the hydrochloric acid salt of imidodiacetic acid, $NH(CH_2COOH)_2$.[1] In order to obtain the free acid, the hydrochloride was dissolved in water and digested with an excess of silver oxide. The silver chloride was filtered off and then the excess of silver removed with hydrogen sulphide. When the solution was evaporated a beautiful crop of colorless prisms separated, which decomposed, with violent effervescence, at 235°–236°. The compound possessed the properties of an acid and a base and agreed in its chemical behavior with the imidodiacetic acid described by Heintz[2] and Eschweiler.[3] Eschweiler states that this acid melts, with decomposition, at about 225°. It has also been our experience that this decomposition point is not definite and varies according to the rate of heating. Analysis (Kjeldahl) :

	Calculated for $C_4H_7O_4N$.	Found.
N	10.5	10.14

2-Ethoxy-4-benzenesulphonyl-6-ketopiperazine,



.—This derivative was obtained when ethyl iodide was allowed to act, at ordinary temperatures, in ether, on the silver salt of 2,6-diketo-4-benzenesulphonylpiperazine. After standing for 24 hours the silver iodide was filtered off and the ether solution evaporated to dryness. The ethyl derivative crystallized from alcohol in pyramids and melted sharply at 130°–132°. Analysis (Kjeldahl) :

	Calculated for $C_{12}H_{14}O_4N_2S$.	Found.
N	9.9	9.76

Some of this ethoxy derivative was heated in a sealed tube,

[1] Ann. Chem. (Liebig), 136, 213.
[2] *Ibid.*, 124, 297; 148, 49; 149, 88; 156, 51.
[3] *Ibid.*, 278, 232.

with ethyl iodide, for 2.5 hours, at 150°. No molecular rearrangement to the isomeric nitrogen alkyl derivative took place under these conditions. The unaltered piperazine was obtained, melting at 130°–132°. When mixed with some of the original material the melting point was not lowered.

Benzenesulphonylbenzoylaminoacetonitrile, $C_6H_5SO_2N(COC_6H_5)CH_2CN$.—This nitrile was prepared by suspending the potassium salt of benzenesulphonylaminoacetonitrile in dry benzene and digesting with a molecular proportion of benzoyl chloride, until the reaction was complete. It crystallized from 95 per cent alcohol in radiating needles and melted, to a clear oil, at 110°–112°. Analysis (Kjeldahl):

	Calculated for $C_{15}H_{12}O_3N_2S$.	Found.
N	9.33	9.63

When the nitrile was boiled with concentrated hydrochloric acid it was hydrolyzed to a mixture of benzoic acid and benzenesulphonylaminoacetic acid. On prolonged boiling the benzenesulphonylaminoacetic acid was decomposed into resinous material.

Action of Phosphorus Pentachloride on Benzenesulphonylaminoacetic Acid.—Nine grams of benzenesulphonylaminoacetic acid were suspended in acetyl chloride and a slight excess over 1 molecular proportion of phosphorus pentachloride was added. Hydrochloric acid began to be evolved immediately. The solution was allowed to stand for about 12 hours and a few more grams of phosphorus pentachloride were added. After the solution had been allowed to remain for 24 hours it was filtered and the acetyl chloride and phosphorus oxychloride removed by distilling at 100°, in a vacuum. By this means we obtained a tar which was insoluble in benzene and ligroin. It had a strong odor of benzenesulphonyl chloride. The tar was suspended in benzene and warmed with a liberal excess of aniline, for 6 hours. The benzene solution was then filtered and allowed to evaporate spontaneously. After standing a few days large, well-developed prisms separated, which melted sharply at 109°–110°, to a clear oil. The product was identi-

fied as benzenesulphonylanilide. When the compound was mixed with pure benzenesulphonylanilide the melting point was not lowered. Analysis :

	Calculated for $C_{12}H_{11}O_2NS$.	Found.
N	5.99	5.85

Carbethoxyaminoacetonitrile, $C_2H_3OOCNHCH_2CN$.—This nitrile was obtained as an oil when an aqueous solution of the sulphate of aminoacetonitrile was treated, alternately, in the cold, with sodium hydroxide and ethyl chlorformate. It boiled at 175° (35 mm.). When pure it showed a great tendency to crystallize. It was very soluble in alcohol and benzene. It crystallized from petroleum ether in beautiful, radiating prisms and melted at 48°–50°, to a clear oil, without effervescence. Analysis :

	Calculated for $C_5H_8O_2N_2$.	Found.
N	21.87	21.85

Action of Benzenesulphonylaminoacetic Acid on Pyrocatechol.—Eight grams of pyrocatechol and 13 grams of benzenesulphonylaminoacetic acid were melted together, at 130°. To the fused material were added 15 grams of phosphorus oxychloride and the mixture heated on the steam-bath. Hydrochloric acid was evolved and the mass assumed a deep red color. After the evolution of hydrochloric acid had practically ceased the product was poured upon finely crushed ice. An oil separated which finally solidified. It was soluble in hot water and was deposited, on cooling, as an oil which afterwards solidified. After recrystallizing from alcohol and benzene it was identified as unaltered benzenesulphonylaminoacetic acid, melting at 166°. Analysis :

	Calculated for $C_8H_9O_4NS$.	Found.
N	6.5	6.2

NEW HAVEN, CONN.,
June 20, 1905.

Contributions from the Chemical Laboratory of the University of Michigan.

GRIGNARD SYNTHESES IN THE FURFURAN GROUP.

By W. J. Hale, W. D. McNally and C. J. Pater.

In the course of a series of investigations upon furfuran derivatives our attention has been called to the alcohols of this group. There are, in fact, very few of such compounds known—the only notable case being that of furfuryl alcohol itself.

The Grignard reaction, through the use of the organomagnesium compounds, offers a most serviceable method for preparing these alcohols. Grignard mentions an isolated case of isoamylfurfuryl carbinol,[1] obtained by the action of isoamylmagnesium bromide upon furfuraldehyde. Phenylmagnesium bromide does not react in a similar manner with the aldehyde, but there results only the production of large quantities of diphenyl instead of the anticipated phenylfurfuryl carbinol. It has also been found that benzylmagnesium chloride behaves in the same manner, giving the hydrocarbon dibenzyl.

Turning our attention then from the secondary alcohols, obtainable with difficulty, we find, on the other hand, that the preparation of members of the tertiary class is comparatively easy. For this purpose the esters of pyromucic and dehydromucic acids have been selected. The action of the various organomagnesium compounds upon these esters has served to produce a number of alcohols of varying chemical properties. Owing to the great ease with which hydrochloric and other acids break up such alcohols, their conversion into halides, through the use of phosphorus compounds, is made impossible. In this respect we may compare the action of mineral acids upon the furfuryl alcohol of Wissell and Tollens.[2] As is best shown in diphenylfurfuryl carbinol, this decomposition is often accompanied with the production of a deep green or blue color, while the residue is a dark red resin. Though the furfuryl group is very sensitive to mineral acids, it is much more

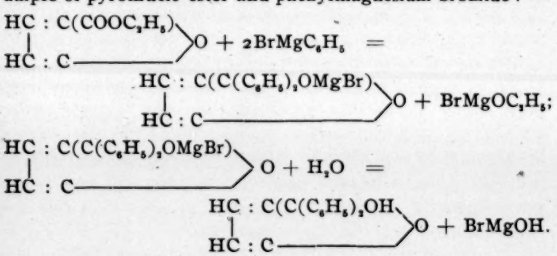
[1] Centrabl., 1901, p. 623.

[2] Ann. Chem. (Liebig), **272**, 295 (1893).

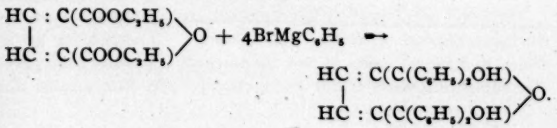
stable when substituted in the α,α'-positions, as in derivatives of dehydromucic acid. None of these alcohols, when perfectly pure, will redden aniline acetate, but, upon standing, the alcohol of the α-furfuryl type slowly undergoes a change, whereby some furfuraldehyde is liberated and hence, upon addition of the aniline salt, the characteristic red color will be developed.

The presence of hydroxyl groups in these alcohols may easily be confirmed by the Tschugaeff reaction,[1] but as a means of further identification, alkyl ethers of the various alcohols were made and analyzed. The method here employed consists in the action of alkyl haloids upon the alkali salts, but is shortened greatly by the use of solid potassium hydroxide with mixtures of the alkyl haloid and the alcohol in question, a method followed by Wissell and Tollens in their work upon furfuryl alcohol. Several attempts were made to prepare esters, as by the use of benzoyl chloride, but only negative results could be obtained, decomposition in most cases having interfered with the process.

The reactions employed may be shown by the following example of pyromucic ester and phenylmagnesium bromide:



In the case of dehydromucic ester we should have, under similar conditions, the following result:



[1] Ber. d. chem. Ges., 35, 3912 (1902).

EXPERIMENTAL.

Diphenyl-α-furfurylcarbinol, $C_4H_3O(C_6H_5)_2 \cdot COH$.—Into a mixture of 15.65 grams brombenzene (2 mols.), and 2.4 grams of magnesium ribbon (2 mols.), all of which had been brought into solution by very gentle boiling for an hour or more under a reflux condenser, on the water-bath, there was gradually added 7 grams (1 mol.) of ethyl pyromucate[1] previously dissolved in dry ether. The reaction takes place almost immediately and, after 3–4 hours' further boiling, a deep, purple color is seen to have developed, while a solid substance separated out. The whole is now treated with cold water to decompose the magnesium compound and enough dilute acetic acid added to effect complete solution of the magnesium salts. To the clear contents of the vessel more ether is added and the ethereal layer removed. The residue obtained from this ether extract was now distilled with steam, in order to remove any unchanged ester or brombenzene that may possibly be present. Only a small amount of diphenyl was seen to collect in the distillate, while from the distilling flask the light brown, solid product was removed and placed upon porous plate to dry. This alcohol may be purified by crystallization from low boiling ligroin (40°–60°). The yield is 70 per cent of the theory. Diphenyl-α-furfuryl carbinol is soluble in ether, alcohol, chloroform, benzene, ethyl acetate, or in warm ligroin, crystallizing from the last in beautiful, colorless, rhombic prisms, melting at 92°.4 (corr.).

0.1752 gram substance gave 0.5222 gram CO_2 and 0.0905 gram H_2O.

	Calculated for $C_{17}H_{14}O_2$.	Found.
C	81.56	81.31
H	5.64	5.78

Diphenyl-α-furfuryl carbinol resembles, in many respects, the furfuryl alcohol of Wissell and Tollens.[2] Though its sensibility to mineral acids is not so marked, it readily undergoes decomposition with dilute hydrochloric acid into a resin-like

[1] Ann. Chem. (Liebig), **28**, 276 (1838).

[2] *Ibid.*, **272**, 295 (1893).

substance. Upon warming this alcohol with hydrochloric acid the green color at first developed passes into a deep purple or violet, a condition more readily obtainable when anhydrous acid is employed. Heating with water at high temperatures effects a decomposition of the alcohol, and even upon standing in the air or in vacuum for a short period the alcohol melts into a gummy mass, acquiring, simultaneously, a dark red color. For a few days this alcohol may be preserved by suspension in ligroin.

Methyl Ether of Diphenyl-α-furfuryl Carbinol, $C_4H_3O(C_6H_5)_2 \cdot COCH_3$.—This ether was prepared in the same manner as furfuryl methyl ether,[1] the simplest of the class of furfuryl ethers. Four grams of the alcohol were dissolved in 5 grams of methyl iodide and to the solution, kept cool by an ice mixture and shaken, there was gradually added 2 grams of finely pulverized potassium hydroxide. The mixture slowly warms up to the boiling-point and is finally removed to a water-bath, where it is gently warmed, under a reflux condenser, till no further action is noticed. A small quantity of water is now added and the alcoholic layer removed by extraction with ether. This ether extract was thoroughly dried over calcium chloride and then a small piece of sodium dropped into it, to unite with any unchanged alcohol. Only the slightest amount of hydrogen escaped, hence the action must have been practically complete. The filtered ether extract was now evaporated and the pleasant smelling product submitted to distillation, *in vacuo*. A colorless oil passes over at 206°–207° (26 mm.). This colorless distillate has sp. gr. 1.1195 at 20°. Upon standing it gradually acquires a yellow color and, like the alcohol itself, is very sensitive to the action of mineral acids, undergoing, thereby, a decomposition into resinous substances. The yield of the ether is quantitative.

0.3092 gram substance gave 0.9280 gram CO_2 and 0.1701 gram H_2O.

[1] Ann. Chem. (Liebig), 272, 296 (1893).

	Calculated for $C_{18}H_{16}O_3$.	Found.
C	81.78	81.86
H	6.09	6.15

Diethyl-α-furfuryl Carbinol, $C_4H_3O(C_2H_5)_2 \cdot COH$.—Into an ethereal solution of ethylmagnesium iodide, prepared from 2.4 grams magnesium and 15.6 grams ethyl iodide, there was gradually added an ethereal solution containing 7 grams ethyl pyromucate. After 3 hours' boiling under a reflux condenser the reaction is completed. The mixture was treated with water containing only enough acetic acid to effect solution and then extracted with ether. The ether extract, freed from the presence of any acid by sodium carbonate and dried over calcium chloride, was allowed to evaporate in a vacuum desiccator. The product obtained could not be purified by distillation, owing to the ease with which it underwent decomposition, but it is undoubtedly the diethyl-α-furfuryl carbinol. It is light yellow in color and possesses a pleasant, ethereal color. Upon standing it was seen to become dark; finally, by placing it in a vacuum desiccator, this color increased in depth until, after a few days, the whole was found to have solidified to a dark brown, crystalline mass, having undergone, therefore, a complete transformation into another derivative.

1-Methyl-2-ethyl-α-furfuryl Ethylene, $C_4H_3OC(C_2H_5) : CHCH_3$.—This ethylene derivative is most naturally to be expected from the foregoing alcohol as the result of dehydration, a condition often brought about in these tertiary alcohols by long standing. The molecule of water thus lost from the hydroxyl group and a hydrogen atom of an ethyl group in the diethylfurfuryl carbinol, may much more readily be eliminated through the agency of gentle heat. In many cases this conversion into unsaturated hydrocarbons has been most effectively carried out through the use of dehydrating agents.[1] Upon crystallization from ethyl acetate the product appeared in fine, long, colorless needles. Several crystallizations quickly made gave a product not so crystalline,

[1] Béhal: Compt. rend., 132, 480 (1901). Tissier and Grignard: *Ibid.*, 132, 1182 (1901). Klages: Ber. d. chem. Ges., 35, 2646 (1902). Hell: *Ibid.*, 37, 225, 230 (1904).

but if the crystallization is carried out slowly the needles at first formed pass over into a second, more stable variety, that of small, colorless, rhombic prisms. This 1-methyl-2-ethyl-α-furfuryl ethylene is soluble in chloroform, benzene, carbon bisulphide, ether or ligroin. It is soluble in warm acetone or ethyl acetate, from either of which it may be crystallized. It is insoluble in water and but sparingly soluble in hot alcohol. A solution of bromine in carbon bisulphide is immediately decolorized by this compound. The best defined rhombic prisms are obtained by crystallization from ethyl acetate and give the constant melting point 249° (corr.).

0.1066 gram substance gave 0.3100 gram CO_2 and 0.0866 gram H_2O.

	Calculated for $C_9H_{12}O$.	Found.
C	79.36	79.31
H	8.88	9.08

The action of methylmagnesium iodide upon pyromucic ester gave a red-colored liquid of pleasant odor, but, owing to its instability, nothing could be done with it.

Dibenzyl-α-furfuryl Carbinol, $C_4H_3O(C_6H_5CH_2)_2 : COH$.—Into an ethereal solution of benzylmagnesium chloride,[1] prepared from 0.96 gram magnesium and 5.04 grams benzyl chloride, there was gradually added 5.6 grams of ethyl pyromucate, dissolved in dry ether. After 3 hours' boiling, under a reflux condenser, upon a water-bath, the reaction was at an end; in the meantime a yellow solid had separated out upon the walls of the flask. The entire contents of the flask were now decomposed with cold water, previously acidulated with acetic acid, and the resulting clear solution extracted with ether. This ethereal extract, freed from its ether, was subjected to distillation by steam for a half hour or more, after which the solid product that collects upon the walls of the vessel was again taken up in ether, the ethereal solution dried over calcium chloride and then allowed to evaporate. Dibenzyl-α-furfuryl carbinol is very soluble in ether, chloroform, benzene, carbon bisulphide, or acetone; fairly soluble in alcohol and insoluble

[1] Ber. d. chem. Ges., 37, 455 (1904).

in water. It is soluble in hot ligroin, from which it crystallizes in beautiful, silky needles showing a constant melting-point of 82°.7 (corr.). This alcohol is much more stable than the corresponding diphenyl derivative. It does not decompose by standing but, through the action of strong hydrochloric acid, rapidly assumes a deep green color, undergoing at the same time complete decomposition.

0.1682 gram substance gave 0.5053 gram CO_2 and 0.1008 gram H_2O.

	Calculated for $C_{19}H_{18}O_2$.	Found
C	81.98	81.94
H	6.52	6.70

Methyl Ether of Dibenzyl-α-furfuryl Carbinol, $C_4H_3O(C_6H_5CH_2)_2 \vdots COCH_3$.—Into a mixture of 2 grams of the alcohol with 2.5 grams of methyl iodide contained in a flask, kept cool by ice-water, there was gradually added 1 gram of finely pulverized potassium hydroxide. The reaction is conducted in the same manner as described under the preparation of methyl diphenyl-α-furfuryl ether. From the ether extract, as finally obtained, there separated a yellow, crystalline compound. This methyl ether is extremely soluble in all of the ordinary media, though but fairly soluble in warm alcohol and insoluble in water. It may, however, with care, be crystallized from low boiling ligroin (40°–60°) in which it dissolves by gentle warming. The crystals appear in long, colorless needles, melting at 61°.2 (corr.).

0.1505 gram substance gave 0.4524 gram CO_2 and 0.0956 gram H_2O.

	Calculated for $C_{20}H_{20}O_2$.	Found.
C	82.15	81.99
H	6.90	7.10

Tetraphenyl-α,α′-furfuryl Dicarbinol, $C_4H_3O:[C(C_6H_5)_2OH]_2$. —Into an ethereal solution of phenylmagnesium bromide, containing 2.4 grams of magnesium and 15.7 grams of brombenzene, there was gradually added 5.3 grams ethyl dehydromucate,[1] dissolved in dry ether. After boiling the contents of

[1] Ann. Chem. (Liebig), **193**, 190 (1878).

the flask over a water-bath for some 4 hours and allowing it to stand over night, a sufficient quantity of water, containing acetic acid, was added and the whole thus brought into solution. The ethereal layer, upon decantation, was freed from ether and distilled with steam, in order to remove any unchanged ester that may be present; in this case only small quantities of diphenyl were collected in the distillate. The yellow mass remaining in the distilling flask was now taken up in ether and the ethereal solution warmed with a small amount of bone-black, filtered, dried over calcium chloride and allowed to evaporate; a light yellow residue was obtained, amounting to about 60 per cent of the theoretical yield. Tetraphenyl-α,α'-furfuryl dicarbinol is soluble in alcohol, ether, acetone, or chloroform, readily soluble in benzene and almost insoluble in ligroin. It dissolves easily in hot carbon bisulphide, crystallizing out on cooling. It is insoluble in water. From solution in ether and ligroin, its best solvent, there is thrown out, upon spontaneous evaporation, small, colorless, rhombic crystals. These, after several crystallizations, melted at 165°.5 (corr.) to a pure, red liquid. This alcohol is more stable than the corresponding diphenyl-α-furfuryl carbinol. It may be preserved for some time, though, on standing, it soon acquires a distinct yellow color. Strong mineral acids decompose it, but not with the same ease with which they act upon diphenyl-α-furfuryl carbinol.

0.2207 gram substance gave 0.6722 gram CO_2 and 0.1126 gram H_2O.

	Calculated for $C_{29}H_{24}O_2$.	Found.
C	83.30	83.07
H	5.59	5.71

Methyl Ether of Tetraphenyl-α,α'-furfuryl Dicarbinol, $C_4H_2O:[C(C_6H_5)_2OCH_3]_2$.—In the same manner as described under the preparation of diphenyl-α-furfuryl carbinol ether, 2 grams of tetraphenyl-α,α'-furfuryl dicarbinol were treated with an excess of methyl iodide (5 grams) and potassium hydroxide (2 grams). The dry ether extract was allowed to evaporate *in vacuo* as, otherwise, only a viscous mass could be obtained.

The crystalline residue could most readily be freed from impurities by digesting it, in the cold, with low boiling ligroin (40°–60°). The remaining portion was next taken up in warm ligroin of the same boiling-point and the solution set in a vacuum desiccator to crystallize. In this manner a white product appeared which, after several similar crystallizations, gave the pure methyl ether. This methyl ether is very soluble in chloroform, ether, benzene, acetone, carbon disulphide, or high boiling ligroin. It is sparingly soluble in low boiling ligroin or alcohol and insoluble in water. The pure ether crystallizes best from alcohol, in white needle clusters, melting at 88°.2 (corr.). When exposed to the air it gradually melts to an indistinct mass.

0.1298 gram substance gave 0.3966 gram CO_2 and 0.0742 gram H_2O.

	Calculated for $C_{28}H_{22}O_2$.	Found.
C	83.44	83.33
H	6.13	6.39

Ethyl Ether of Tetraphenyl-α,α'-furfuryl Dicarbinol, $(C_4H_3O) : [C(C_6H_5)_2OC_2H_5]_2$.—By the action of potassium hydroxide upon a solution of tetraphenyl-α,α'-furfuryl dicarbinol, in ethyl iodide, in accordance with the method described in the preparation of the previous ethers, the ethyl ether of this alcohol was readily obtained. The product has a fine, crystalline appearance and is very soluble in alcohol, ether, acetone, or chloroform ; fairly soluble in benzene or carbon bisulphide ; insoluble in water and almost insoluble in ligroin. It may best be crystallized out of ether and ligroin, from which it appears in rhombic prisms, melting at 171° (corr.). The ethyl ether is a much more stable compound than the corresponding methyl ether. Upon standing it slowly acquires a distinctive yellow color and, when melted, undergoes decomposition into a red product.

0.1489 gram substance gave 0.4564 gram CO_2 and 0.0899 gram H_2O.

	Calculated for $C_{34}H_{32}O_3$.	Found.
C	83.56	83.60
H	6.60	6.75

The preparations of tetraethyl- and tetramethyl-α,α'-furfuryl dicarbinols were attempted but the light red colored liquids obtained could not be satisfactorily worked up. They possessed a most pleasant ethereal odor and slowly underwent decomposition, even at ordinary temperatures.

Tetrabenzyl-α,α'-furfuryl Dicarbinol, $C_4H_2O : [C(C_6H_5CH_2)_2OH]_2$.—Into a solution of benzylmagnesium chloride, prepared from 2.3 grams magnesium and 12 grams of benzyl chloride, in dry ether, an ethereal solution of 5 grams of ethyl dehydromucate was slowly added. After some 3 hours' boiling upon the water-bath the reaction is at an end, the product was allowed to stand a short time and was then decomposed, in the usual way, with water containing acetic acid. The whole was then extracted with ether, which, in turn, must be freed from any acid by sodium carbonate and then dried over calcium chloride. The residue from the ether extract was now submitted to distillation with steam for a short time, to remove any unchanged ester and the dibenzyl usually present. The yellow substance thus left in the distilling flask was again taken up in ether, treated with bone-black, dried over calcium chloride and then allowed to evaporate in a vacuum desiccator. The residue was an extremely viscous mass, which refused to crystallize even after long standing. Application of low temperature easily brought about a solidification, but not in the crystalline form. This solid product becomes viscous again at 5°–6°. Tetrabenzyl-α,α'-furfuryl dicarbinol is a fairly stable alcohol, of a light straw color, possessing a very agreeable odor. It is soluble in all the ordinary media excepting ligroin and water. From mixtures of ligroin with the other solvents no crystalline product could be obtained, in every case the deposited substance was viscous. The alcohol boils at 193°–195° (30 mm.) but, as a great portion hereby undergoes decomposition, only a small

quantity of pure product can be collected. The sp. gr. of the alcohol is 1.126 at 27°.

0.1758 gram substance gave 0.5374 gram CO_2 and 0.1046 gram H_2O.

	Calculated for $C_{21}H_{32}O_2$.	Found.
C	83.56	83.38
H	6.60	6.66

ANN ARBOR, MICH.,
July 22, 1905.

SOME CONCENTRATION CELLS IN METHYL AND ETHYL ALCOHOLS.

BY J. HUNT WILSON.

Although within the last two decades measurements of concentration cells, for the purpose of verifying the equations of Nernst and Planck, have been numerous, such measurements have been almost wholly restricted to aqueous solutions. Up to the present time I have been unable to find any measurements recorded of a non-aqueous concentration cell. Jones[1] measured some cells of the type

$$\mathrm{Ag}\left|\begin{array}{c}\mathrm{AgNO_3}\\ \text{in}\\ \text{water}\\ \frac{N}{10}\end{array}\right|\left|\begin{array}{c}\mathrm{AgNO_3}\\ \text{in}\\ \text{alcohol}\\ \frac{N}{10}\end{array}\right|\mathrm{Ag},$$

in an attempt to calculate the percentage of ionization in the alcoholic solutions, but found that the solution tension of Ag has a value much smaller in alcoholic solutions than in water. He calculated the ratio to be about 1 : 42 to 1 : 48.

Campetti[2] gives the results of some measurements similar to those of Jones. He worked with solutions of NH_4Cl, LiCl, $ZnCl_2$, $CuCl_2$, $CdCl_2$, ZnI_2, CdI_2, in both water and alcohol. To determine the potential differences he made use of the "dropping electrode." He states, as did Jones, that the alcoholic solution is positive in reference to the aqueous solution.

[1] Z. physik. Chem., 14, 346.
[2] *Ibid.*, 14, 374.

My object in taking up the following work was to determine the electromotive force of a few non-aqueous concentration cells.

As the formula of Nernst is based on the theory of electrolytic dissociation, its ability to predict the electromotive force of a non-aqueous concentration or liquid cell would largely depend on the extent to which the theory of ionization could be applied to such solutions. Restricted to aqueous solutions, the theory of electrolytic dissociation serves to correlate and explain observed phenomena very clearly, but its extension to non-aqueous solutions has, in many instances, given rise to anomalies which can only be harmonized with the theory by the introduction of ideas of the association of both solvent and solute and of combination between both. In all cases, however, it serves as an admirable "working hypothesis."

Two formulas are available for calculating the electromotive force of a concentration cell. The first of these, that of Helmholtz, is independent of the ionic theory and calculates the electromotive force from the vapor pressures of the two solutions of the cell. The formula of Nernst is based on the ionic theory, and involves a knowledge of the transport numbers of the dissolved substance and of the osmotic pressures of the solution. In the formula

$$\pi = 0.0002 \frac{2v}{u+v} \cdot T \cdot \log \frac{p_1}{p_2}$$

the ratio $\frac{p_1}{p_2}$ is commonly set equal to the ratio of the molecular concentration. In dilute, aqueous solutions this is approximately correct, but in concentrated, aqueous solutions and in non-aqueous solutions of low ionizing power, it would cause a large error due to incomplete dissociation. In such cases the ratio of the ionic concentrations as calculated from the conductivities is substituted for the ratio of the osmotic pressures.

The choice of a non-aqueous concentration cell for measurement and calculation of its electromotive force is rather diffi-

cult. While of late years measurements of the conductivities of non-aqueous solutions have been numerous, there are very few compounds, the transport numbers of which are known for a non-aqueous solvent. Silver nitrate is soluble, however, in both methyl and ethyl alcohol, and as values of the conductivities and transport numbers of this salt are available for these solvents, I have undertaken the measurement of some cells of the type

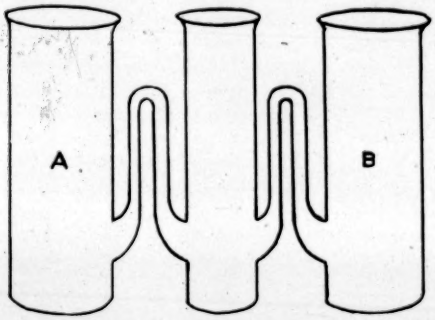
$$\mathrm{Ag}\left|\begin{array}{c|c}\mathrm{AgNO_3}\ \text{in alcohol}\ \frac{N}{10} & \mathrm{AgNO_3}\ \text{in alcohol}\ \frac{N}{100}\end{array}\right|\mathrm{Ag}.$$

EXPERIMENTAL PART.

All the methyl and ethyl alcohol used in the following work was purified by distillation from lime, anhydrous copper sulphate and, finally, from sodium. Even alcohol thus purified gave a slight discoloration with silver nitrate, but I found that, by distilling with a small quantity of silver nitrate, a product was obtained which gave a clear solution. The silver nitrate used was crystallized from water, dried, fused at a gentle heat and then powdered. In distilling the alcohols and in preparing the solutions, moisture was excluded as far as possible by the use of tubes filled with phosphorus pentoxide. All the measurements of electromotive force were made by the compensation method, with a D'Arsonval galvanometer as zero instrument. The vessel used to contain the cells was of the form on the opposite page.

The siphon tubes from each half cell were fused into a connecting vessel instead of being immersed in it, as this facilitated the exclusion of moisture and made the cell more compact and easier to handle in the thermostat. The top of each tube was closed by means of a tightly-fitting rubber stopper, through which passed a drying tube filled with phosphorus pentoxide. The electrodes were of silver foil and were coated with electrolytic silver before use. The glass tubes carrying the electrodes were pushed through the rubber stoppers of the tubes designated A and B in the figure.

For the measurements at 25° the cell was placed in an Ostwald thermostat, for those at 0° it was packed in finely crushed ice. Solutions of silver nitrate, in methyl alcohol, of four



different concentrations were made up. The first solution was prepared by direct weighing, the others by diluting portions of the original solution. The following table gives the concentration, in liters per gram-molecule (v) and the molecular conductivity μ, at both 25° and 0°. The values of the conductivities are taken from the recent work of Jones and Bassett :[1]

v.	μ_v 0°.	μ_v 25°.
10	25.96	35.77
40	39.71	53.42
160	51.09	70.36
640	61.42	88.24

Concentration cells were then prepared with these various solutions and their electromotive force measured. In the following tables v'-v'' represent the concentrations of the two solutions used in the cell, b the observed electromotive force, and c the value of the electromotive force calculated from the formula of Nernst :

[1] This Journal, 33, 430.

At 25°.

v'–v''.	*b.*	*c.*
10–40	0.021	0.029
—160	0.044	0.062
—640	0.086	0.098
40–160	0.031	0.033
—640	0.065	0.068
160–640	0.035	0.034

At 0°.

v'–v''.	*b.*	*c.*
10–40	0.018	0.026
—160	0.034	0.057
—640	0.067	0.090
40–160	0.028	0.032
—640	0.061	0.064
160–640	0.031	0.033

In calculating the above results allowance was made for incomplete dissociation by introducing the ratio of the ionic concentration into the formula in place of the molecular concentrations. The value of the ionic concentration was obtained from the expression $\frac{\mu_v}{\mu\infty} \times m$, where $\frac{\mu_v}{\mu\infty}$ represents the degree of dissociation and m the molecular concentration.

Solutions of silver nitrate in ethyl alcohol were then prepared of the following concentrations:

v.	μ_v 0°.	μ_v 25°.
38.86	11.35	16.96
155.47	15.13	23.87
621.89	19.43	30.62

These values are also taken from the results of Jones and Bassett.[1] Cells were made up and measured as previously described:

At 25°.

Cell.	*b.*	*c.*
38.86–621.89	0.067	0.067
—155.47	0.029	0.032
155.47–621.89	0.038	0.035

[1] *Loc. cit.*

At 0°.

Cell.	*b.*	*c.*
38.86–621.89	0.055	0.062
—155.47	0.027	0.032
155.47–621.89	0.035	0.031

A close comparison between the observed and calculated values will show that the agreement is quite good in most cases. With the exception of the cells containing N/10 $AgNO_3$ in methyl alcohol the difference between the observed and calculated values is less than 0.05 volt, except in the first ethyl alcohol cell measured at 0°, where there is a difference of 0.07 volt. With these exceptions the agreement of values is fully as good as is commonly obtained with aqueous solutions.

Before attempting to account for the poor agreement in N/10 methyl alcohol cells it would be advisable to confirm these values by additional measurements, although it is hardly possible that the difference is due to experimental errors, as all the measurements were made in duplicate.

It should be stated here that the Nernst formula can hardly be regarded as giving more than approximate values. The formula presupposes the absence of any molecular aggregation of dissolved molecules, or any combination between solvent and solute. These phenomena are of common occurrence in both aqueous and non-aqueous solutions. Also, when we consider the uncertainty of the value of $\mu\infty$ for both alcohols, the above agreement must be considered satisfactory.

In the calculation values given above, 98 was taken as the value of $\mu\infty$ for silver nitrate in methyl alcohol, while 35.5 was used as the most probable value of $\mu\infty$ in the ethyl alcohol solutions.[1]

From the results obtained in this work I am led to believe that the Nernst formula will be found to hold as well in non-aqueous as in aqueous solutions, but more extensive measurements of non-aqueous concentration cells are necessary before this can be assured. In the near future I hope to publish some measurements of concentration cells with pyridine as the solvent.

[1] Jones: Z. physik. Chem., 14, 354.

In conclusion, I desire to express my thanks to Dr. C. J. Thatcher for valuable suggestions and criticism during the course of this work.

EASTON, PA.,
July 20, 1905.

A PERIODIC RELATION BETWEEN THE ATOMIC WEIGHTS AND THE INDEX OF REFRACTION.

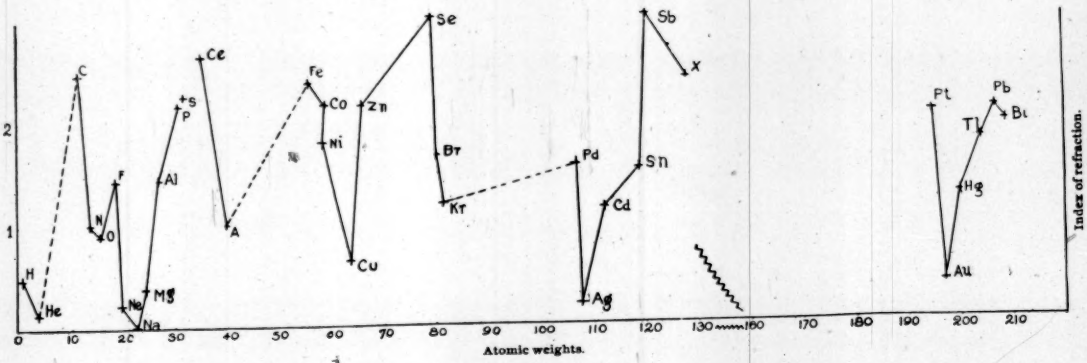
BY F. L. BISHOP.

The absolute establishment of a periodic relation between the atomic weights and the index of refraction would require the accurate determination of the index of refraction for a number of elements which have never been investigated. However, Professor Paul Drude[1] has made a study of the index of refraction of many of the opaque elements, while for the transparent bodies there are, in most instances, numerous determinations. In the case of gases the refractivity has been accurately determined by the method suggested by Lord Rayleigh.[2]

The data at present available for illustrating this periodic relation are given in the following table, where the elements are arranged in the order of increasing atomic weights:

Element.	Atomic weight.	Index.
H	1.008	0.473
He	4.00	0.124
C (diamond)	12.00	2.46
N	14.04	1.02
O	16.00	0.924
F	19.00	1.434
Ne	20.00	0.235
Na	23.05	0.005
Mg	24.36	0.373
Al	27.1	1.44
P	31.0	2.14
S	32.0	2.24
Cl	35.45	2.62
A	39.9	0.968
Fe	55.9	2.36

[1] Wied. Ann., **39**, 513 (1890).
[2] P. Roy. Soc., **59**, 206 (1895).


H
He
C
N
O
F
Ne
Na
Mg
Al
Si
P
Ce
A
Fe
Co
Ni
Cu
Zn
Se
Br
Kr
Pd
Ag
Cd
Sn
Sb
X
Pt
Au
Hg
Tl
Pb
Bi
1
2
0
10
20
30
40
50
60
70
80
90
100
110
120
130
160
170
180
190
200
210
Atomic weights.
Index of refraction.

Element.	Atomic weight.	Index.
Ni	58.7	1.79 } ?
Co	59.0	2.12 }
Cu	63.6	0.641
Zn	65.4	2.12
Se	79.2	2.98
Br	79.96	1.65
Kr	81.8	1.45
Pd	107.0	1.54 *red*
Ag	107.93	0.181
Cd	112.4	1.13
Sn	119.0	1.48
Sb	120.2	3.04
X	128.0	2.36
Pt	194.8	2.06
Au	197.2	0.366
Hg	200.0	1.73
Tl	204.1	1.75
Pb	206.9	2.01
Bi	208.5	1.90

The index is that of sodium light at 20°, and the gases are under standard pressure.

The values obtained by Drude are used, even when later determinations are available, in order that the same instrumental errors may be present.

The maxima and minima are best studied from the curves (*vide* p. 85).

It is seen that the minima of the well defined groups are Na, Cu, Ag, Au, which are metals in the first group of Mendeléeff's periodic table. The periodicity is, perhaps, best shown in the series from C to Cl, as we have in this series the index for all the elements.

It is evident from the methods of measurement of the index for opaque substances that there is opportunity for more or less error, it is not the purpose of this preliminary note, however, to discuss methods, but to note the apparent periodic relation between the atomic weights and the index of refraction of the elements.

PHYSICAL LABORATORY,
BRADLEY POLYTECHNIC INSTITUTE.

NOTE.

The Preparation of Benzonitrile.

In the course of some work which was being carried out in this laboratory in 1904, it was necessary to provide rather large quantities of benzonitrile; at my suggestion, therefore, Messrs. E. J. Hoffman, and W. A. Syme studied some of the various methods which have been proposed for the preparation of this compound. Their results, which may be of use to others, are recorded in the following table; they have been checked, in most cases, by other students. The figures given for the cost are believed to be accurate *relatively*, the *absolute* cost is, necessarily, variable. In reckoning the time no account was taken of the washing and distillation of the crude product, as this was practically the same in all cases; the time required to dry an ethereal solution, when this was needful, has also been disregarded, because it did not occupy the worker. The yield refers to material which has been distilled.

Method I.—Sandemeyer's reaction:[1] Aniline 35 grams, copper sulphate crystals 100 grams, potassium cyanide 110 grams, sodium nitrite 25 grams and hydrochloric acid 50 grams were employed.

Method II.—From benzamide 15 grams and phosphoric anhydride 25 grams.[2]

Method III.—From benzoic acid 100 grams and lead thiocyanate 240 grams.[3]

Method IV.—From sodium benzenesulphonate 100 grams and potassium cyanide 100 grams.[4]

Method V.—From benzamide 23 grams and quicklime in excess.[5]

Method VI.—From benzoic acid 50 grams and potassium thiocyanate 20 grams.[6]

As was to be expected Mr. Syme did not obtain a large yield of benzonitrile by the use of iodobenzene and silver cyanide,[7] nor was he able to get satisfactory results by the distillation of aniline oxalate.[8] He prepared benzamide very easily and quickly from benzoic acid and ammonium thiocyanate.[9]

[1] Ber. d. chem. Ges., **17**, 2653.
[2] Hofmann and Buckton: Ann. Chem. Pharm., **100**, 155.
[3] Krüss: Ber. d. chem. Ges., **17**, 1766.
[4] Merz: *Ibid.*, **3**, 710.
[5] Anschütz and Schulz: Ann. Chem. Pharm., **196**, 48.
[6] Letts: Ber. d. chem. Ges., **5**, 673.
[7] Merz and Weith: *Ibid.*, **10**, 746.
[8] A. W. Hofmann: Compt. rend., **64**, 388.
[9] Kekulé: Ber. d. chem. Ges., **6**, 113.

Method.	Yield. Grams.	Per cent of the theoretical.	Time.	Cost of 100 grams.
I	25	64	About 4 hours	$0.72
II	12	95	" 1 "	$1.00
III	60	71	" 10 "	$0.55
IV	15	26	" 1 "	$5.86
V	8.2	42	1 "	$1.70
VI	12.2	58	3 "	$1.15

J. BISHOP TINGLE.

JOHNS HOPKINS UNIVERSITY,
January, 1905.

REPORTS.

The Rusting of Iron.

In presenting the subject of chemistry to a class just beginning the study of that science, the rusting of iron is often given as an example of a familiar chemical action. The commonly accepted explanation of this change is that given by Grace Calvert and Crum Brown. According to these authors it is due to the combined action of the oxygen and carbon dioxide of the air in the presence of liquid water and should be represented by the following equations:

$$4Fe + 4H_2O + 4CO_2 = 4FeCO_3 + 4H_2;$$
$$4FeCO_3 + 6H_2O + O_2 = 2Fe_2(OH)_6 + 4CO_2.$$

In a recent paper[1] Dunstan, Jowett and Goulding show that the action does not require the presence of carbon dioxide and that the inhibiting action of alkalies is not due to their power of absorbing this substance. The results show that, although hydrogen peroxide cannot actually be detected during the rusting of iron, it is probably formed as an intermediate product of the change. The results of these experiments support Traube's view of the nature of such oxidation processes, *viz.*, that the water is decomposed by the iron, the liberated hydrogen forming hydrogen peroxide with the dissolved molecular oxygen, involving the assumption that hydrogen peroxide is not "oxidized water," but "reduced or hydrogenized oxygen." According to the authors the reactions involved should be represented by the equations:

$$Fe + O_2 + H_2O = FeO + H_2O_2;$$
$$2FeO + H_2O_2 = Fe_2O_3.H_2O.$$

[1] J. Chem. Soc., 88, 1548 (1905).

The excess of hydrogen peroxide immediately reacting with the iron to form a further quantity of rust thus:

$$Fe + H_2O_2 = FeO + H_2O ;$$
$$2FeO + H_2O_2 = Fe_2O_3.H_2O.$$

It is shown, in support of this theory, that many substances which decompose hydrogen peroxide and therefore interfere with its existence, likewise prevent the rusting of iron, while bodies which are incapable of decomposing hydrogen peroxide do not prevent the rusting. In the atmospheric oxidation of lead and zinc the formation of hydrogen peroxide has been actually detected, and the substances which prevent the action in the case of iron act in a similar manner with lead and zinc. Parallel series of experiments, when the duration of the experiments was as much as 3 months, show that iron does not rust when left in contact with dry gases, nor does it rust when in contact with moist oxygen or a mixture of moist oxygen and carbon dioxide so long as the temperature is kept constant, whereby the deposition of liquid water on the metal is prevented. With a fluctuating temperature it rusts in moist oxygen, and in a mixture of moist oxygen and carbon dioxide; but not in carbon dioxide alone nor in a mixture of moist oxygen and ammonia. Whitney supposed the rusting to be due to a slight dissociation of the water into H and OH ions and to a solution of minute quantities of iron, owing to the formation of an electric circuit, to form ferrous hydroxide which would absorb oxygen from the air. If this explanation is correct the hydrogen should escape as a gas and substances such as alkalies, by hindering the accumulation of H ions, should interfere with rusting or entirely prevent it, while acids and some salts should accelerate it, as they increase the accumulation of H ions. The authors, however, could obtain no evidence of the formation of hydrogen and proved that substances such as chromic acid prevent the rusting; they also showed that if part of the water which had been in contact with iron for 3 weeks, without any visible change having taken place, was quickly poured off when the vessel was opened, and was then allowed to stand in the air, no precipitation of iron salts took place nor could any trace of iron be detected in the solution, while the iron which was left in the water quickly rusted when air was allowed to come in contact with the water covering the iron.

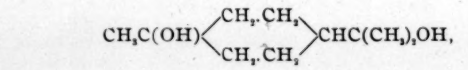
A study of the action of carbon dioxide under different conditions, including a repetition of Grace Calvert's work, showed that the small amount of carbon dioxide in the air could

play only a very subordinate part in the ordinary rusting of iron, especially as it has been proved that rusting proceeds rapidly in the total absence of carbon dioxide.

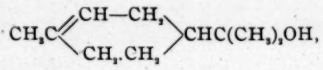
The authors demonstrated that the process of "rusting" is different from other processes in which iron undergoes oxidation with the formation of ferric hydroxide, and conclude, therefore, that iron, oxygen and *liquid* water are alone necessary for the rusting of iron. J. E. G.

Grignard's Reaction.

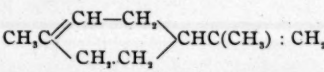
Since the publication of the previous report,[1] papers dealing directly or indirectly with this subject have appeared in scarcely lessened numbers; only the more important of them will be referred to in the present communication. W. H. Perkin, Jr.,[2] has synthesized terpin,



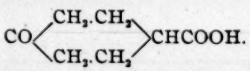
terpineol,



and dipentene (limonene),

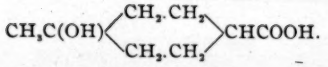


by the following steps: Ethyl β-iodopropionate and ethyl sodiocyanoacetate yield ethyl γ-cyanopentane-α,γ,ϵ-tricarboxylate, $C_2H_5OCOC(CN)(CH_2CH_2COOC_2H_5)_2$; concentrated hydrochloric acid converts this into pentane-α,γ,ϵ-tricarboxylic acid, $HOCOCH(CH_2CH_2COOH)_2$, which, when digested with acetic anhydride and distilled, passes into δ-ketohexahydrobenzoic acid,

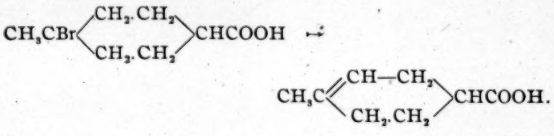


The ester of this acid is treated with methylmagnesium iodide and the product hydrolyzed, when there is obtained δ-hydroxyhexahydroparatoluic acid,

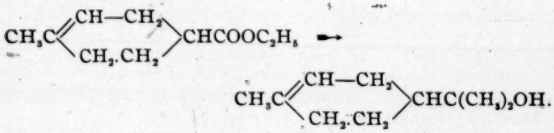
[1] THIS JOURNAL, 33, 304 (1905).
[2] J. Chem. Soc., 85, 654 (1904).



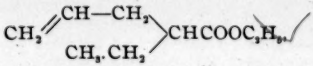
Fuming hydrobromic acid converts this into the corresponding bromo acid which, under the influence of pyridine, passes into Δ^3-tetrahydroparatoluic acid,



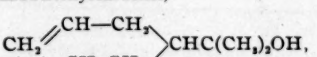
From the ester of the unsaturated acid methylmagnesium iodide yields terpineol,



Terpineol is readily converted into dipentene and terpin hydrate by the action of potassium hydrogen sulphate and dilute sulphuric acid, respectively. Apart from its other interest, this synthesis may be regarded as settling, beyond dispute, the question of the constitution of the three hydrocarbons concerned. In subsequent papers,[1] Perkin and his co-workers describe syntheses of other, hitherto unknown, terpenes, by the same series of reactions using Δ^1-tetrahydroparatoluic acid, and also the preparation, from ethyl allylacetate, of the open chain compounds, ethyl ethylallylacetate,

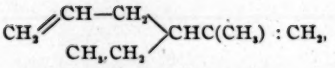


dimethylethylisobutenylcarbinol,

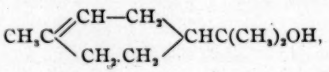


and ethylallylisopropenylmethane,

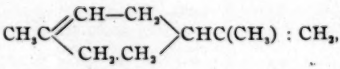
[1] J. Chem. Soc., **87**, 639, 655 (1905).



the object being to compare their properties with those of terpineol,

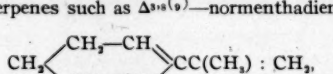


and dipentene,

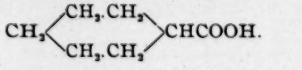


respectively. The conclusion is drawn that, although the open chain compounds show certain similarities in behavior to the terpenes and their derivatives, yet the closed chain structure has a distinct influence on the properties of the terpenes.

In his next paper[1] a description is given of the synthesis of a number of terpenes such as $\Delta^{3,8(9)}$—normenthadiene,

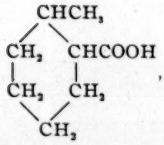


which do not contain the paramethyl group that is so characteristic of the natural terpenes. The starting point in the synthesis was hexahydrobenzoic acid,

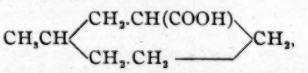


It is well known that the natural terpenes and allied compounds are almost exclusively derivatives of paracymene, or are easily converted into such derivatives. In the last two papers[2] of the series under consideration, the synthesis of terpenes derived from orthocymene and from metacymene is described. In general properties these resemble the para compounds. The starting points for the preparations were *trans*-hexahydroorthotoluic acid,

[1] J. Chem. Soc., 87, 661 (1905).
[2] *Ibid.*, 87, 1066, 1083 (1905).



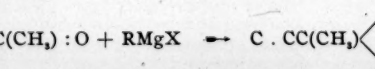
and hexahydrometatoluic acid,



respectively, the methods and reactions being similar to those described in the earlier portion of this report (p. 90).

In a series of interesting papers[1] on the reaction of alkyl magnesium halides with various unsaturated compounds. Kohler and his fellow workers have discovered the following regularities: (1) The magnesium derivative invariably adds itself to the carbonyl group of unsaturated aldehydes,

this gives, ultimately, the carbinol C:CCHROH. (2) Unsaturated ketones containing the group CH_3CO react like aldehydes,



(3) Unsaturated ketones containing the group C_6H_5CO add the magnesium reagent in the positions 1,4,

$$C:CC(C_6H_5):O + RMgX \rightarrow CRC:C(C_6H_5)OMgX \rightarrow CRC:C(C_6H_5)OH.$$

(4) The esters of unsaturated acids react both by 1,4 addition and by the replacement of alkyloxyl by alkyl:

(i) $C:C(OR):O + R'MgX \rightarrow R'CC:C(OR)OMgX \rightarrow R'CC:C(OR)OH$;

(ii) $C:CC(OR):O + R'MgX \rightarrow C:CC(R'):O + BrMgOR.$

[1] THIS JOURNAL, **31**, 643; **33**, 21, 35, 153, 333; **34**, 132, 570.

The first equation represents the principal reaction of aromatic magnesium compounds with such esters, the second that of aliphatic magnesium compounds, but the result is also somewhat dependent on the nature of the atoms or groups in the α-position to the carbonyl, negative groups increase the extent of the additive action.

The application of the Grignard reaction has received further extensions by three noteworthy improvements in its technique. The earlier users of the Grignard reagent regarded the ether which was employed in its preparation as being merely an indifferent solvent, but it was speedily recognized, by Grignard himself[1] and also by Blaise,[2] that the reaction between magnesium and the alkyl haloid would not take place in the absence of ether; the latter was, therefore, assumed to be present in the resulting compound as "ether of crystallization." W. Tschelnizeff[3] has carried out a series of experiments which show that, although alkyl haloids and magnesium do not react in the absence of ether at the temperatures usually employed, they will do so at higher ones, for instance in vigorously boiling benzene, or better, in toluene solution. The ether, therefore, acts simply as a typical catalytic agent and an extremely small amount of it is sufficient to bring about the formation of the Grignard reagent at the ordinary temperature. It thus becomes possible to prepare the reagent and carry out the subsequent reaction in a solvent other than ether, whereby the upward limit of temperature which may be employed is raised. The same author had shown, in a previous paper,[4] that a tertiary base, such as dimethylaniline, could take the place of the ether in the Grignard synthesis and that, in some cases, such a substitution was of practical advantage. In a later paper[5] he records the results of his determination of the "heats of formation" of a number of Grignard reagents from ether and various organomagnesium halides. The experiments were carried out by mixing magnesium powder with excess of the alkyl haloid, adding a neutral solvent, usually benzene, and then a few drops of dimethylaniline to act as a catalyst; when the reaction was completed a known excess of ether was poured in and the resulting evolution of heat was measured. These experiments, as well as his previous work, lead the author to the conclusion that Grignard's reagent is an oxonium compound, as suggested by Baeyer and Villiger,[6]

[1] Dissertation, University of Lyons, 1901.
[2] Compt. rend., **132**, 839.
[3] Ber. d. chem. Ges., **38**, 4534 (1904).
[4] *Ibid.*, **37**, 2081 (1904).
[5] *Ibid.*, **38**, 3664 (1905).
[6] *Ibid.*, **35**, 1201 (1902).

and that its formation is represented by the following equations:

$$Mg + RX \rightarrow MgRX;$$

$$MgRX + (C_2H_5)_2O \rightarrow \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!O\!<\!\!\begin{matrix} MgR \\ X \end{matrix}$$

The reaction is, of course, similar if a tertiary base such as dimethylaniline, is employed instead of ether,

$$MgRX + C_6H_5N(CH_3)_2 \rightarrow C_6H_5{-}N\!<\!\!\begin{matrix} X \\ CH_3 \\ CH_3 \\ MgR \end{matrix}$$

In the course of their investigations of triphenylcarbinol derivatives, Baeyer and Villiger[1] were unable to obtain magnesium derivatives of brom- or iodoaniline or of the corresponding dimethylanilines. Sachs and Ehrlich,[2] who had encountered the same difficulty, overcame it, to some extent, by treating the magnesium with ethyl bromide then, as soon as the reaction was well started, the greater portion of the liquid was poured away and parabromdimethylaniline was added; under these circumstances a small portion of dimethylaniline-magnesium bromide was formed which proved to be sufficient for their qualitative purposes, though it was, of course, contaminated with other substances and was unsuited for the preparation of pure derivatives. Baeyer continued his work on the subject and has recently described an extremely simple and beautiful method for the preparation of a highly reactive form of magnesium.[3] Magnesium filings are heated in a flask and half their weight of iodine added gradually. The product forms a dull gray powder, which acts with great energy on water and on methyl alcohol, hydrogen being evolved and magnesium hydroxide and methoxide, supposedly, being formed. The action of ethyl alcohol is feebler and amyl alcohol has no effect on the magnesium compound. The nature of this magnesium halide is not stated, but it is, presumably, a subiodide, possibly similar in composition to Cd_4I_7.[4] At all events it differs markedly in properties from the normal anhydrous magnesium iodide.

The magnesium subiodide is without action on chlor-

[1] Ber. d. chem. Ges., 36, 2775 (1903).
[2] *Ibid.*, 36, 4296 (1903).
[3] *Ibid.*, 38, 2759 (1905).
[4] Morse and Jones: THIS JOURNAL, 12, 491 (1890).

benzene, but it acts energetically on brombenzene and on all the iodoanilines and dimethylanilines, most readily with the ortho derivatives, least so with the para compounds. The use of this reagent has already permitted the preparation of all the possible aminotriphenylcarbinols and there can be no doubt that its employment will prove to be extremely useful in other directions. Although, in the preceding pages, reference has been made to some only of the more interesting points which have been developed recently in connection with Grignard's reaction, sufficient evidence has, perhaps, been offered to demonstrate that this most fruitful and admirable synthetical method still maintains its popularity and that the results obtained by its use show no diminution in their interest and value. J. BISHOP TINGLE.

REVIEWS.

OUTLINES OF INDUSTRIAL CHEMISTRY. By FRANK HALL THORP, PH.D., Associate Professor of Industrial Chemistry in the Massachusetts Institute of Technology. New York: Macmillan Co. 1905. Price, $3.50.

Reviews by Professor Mallett of the previous editions of this work have been published in this JOURNAL.[1] It is only necessary to say that the present edition is enlarged, improved and thoroughly revised, and that the author has added an outline of elementary metallurgy; we consider this edition of Professor Thorp's work a very valuable text-book. E. R.

A TEXT-BOOK OF CHEMICAL ARITHMETIC. By HORACE L. WELLS, M.A., Professor of Analytical Chemistry and Metallurgy in the Sheffield Scientific School of Yale University. First Edition. First Thousand. New York: John Wiley and Sons. 1905. 12mo. vii + 169 pages. Price, $1.25.

This is an excellent book for students of quantitative analysis, for whom it is intended, but it will also be found very useful for beginners. The use of the methods of abbreviated multiplication and division will save much time and many errors.

E. R.

LES NOUVEAUTÉS CHIMIQUES POUR 1905. NOUVEAUX APPAREILS DE LABORATOIRES, METHODES NOVELLES DE RECHERCHES APPLIQUERS A LA SCIENCE ET A L'INDUSTRIE. Avec 180 figures. By CAMILLE POULENC, Docteur des Sciences. Paris: J. B. Ballière et Fils. 1905.

In this, as in the preceding volumes of the series, M. Poulenc gives an illustrated list of all new apparatus and new methods.

[1] THIS JOURNAL, 21, 181; 23, 268.

Much of the apparatus of course is trivial or of doubtful utility, but many useful improvements are described. Some of the methods given in detail are of absorbing interest, such as the methods and apparatus of M. and Mme. Curie for the study of radioactive substances; M. Verneuil's apparatus for the manufacture of artificial ruby; Moissan and Rigaut's apparatus for preparing pure argon; and Wachsmuth's apparatus for determining acoustically the density of gases and vapors.

E. R.

DIE NEUERER ENTWICKELUNG DER KRISTALLOGRAPHIE. Von DR. H. BAUNHAUER. Braunschweig: Fr. Viewieg u Sohn. 1905. pp. 184. Price, M. 4.

The seventh of the Natural History monographs issued by Vieweg und Sohn is an excellent example of the "digestive" works which this series aims to supply. The present volume, though not exhaustive, is complete and well balanced. It is also up-to-date in its discussions of various problems presented by crystallography. It gives a clear, succinct account of the fundamentals of the science, among which it emphasizes the Law of Zones and the Rationality of the Indices. The treatment of geometrical crystallography is good, giving in an orderly but individual way the characteristics of the symmetry properties and crystal classes now recognized by all crystallographers. The means employed for determining the symmetry of crystalline bodies are well described, and the newer work on the formation of twins and crystal growth is well summarized.

Towards the end of the book the author devotes twenty or more pages to the less established conclusions of chemical crystallography. Here the treatment changes from the broader conclusions generally accepted to the conclusions of individual workers and the more specific cases. There is an evident attempt to maintain the same attitude throughout, but the uncertainty in this newer field of investigation is clearly manifest. The relations existing between chemical constitution and crystal structure are hinted at by reference to the fact that compounds like Fe_2O_3, $FeCl_3$, or $CaCl_2.6H_2O$, show trigonal or hexagonal symmetry while $ZrSiO_4$, $BeSO_4.4H_2O$ and others are tetragonal. It is, however, manifestly too early to draw serious conclusions on these problems.

The book is unusually good in its place. It is not a textbook for the beginner, nor a treatise for the advanced student, but for those who have some knowledge of crystallography and wish to keep abreast of the advances made in that science it can hardly be excelled.

EDWARD B. MATHEWS.

A TREATISE ON CHEMISTRY. By SIR H. E. ROSCOE, F.R.S., AND C. SCHORLEMMER, F.R.S. Volume I. The Non-Metallic Elements. New edition completely revised by Sir H. E. Roscoe assisted by Drs. H. G. Coleman and A. Harden, with 217 illustrations and a portrait of Dalton engraved by C. H. Jeens. London and New York: Macmillan & Co. 1905. pp. 931.

The new edition of "Roscoe and Schorlemmer" is of special interest to chemists at the present time, for with the exception of Dammer's "Handbuch," which has a supplementary volume reporting progress up to 1903, there is no large manual, in English, French or German at least, which includes the work of the past ten years in inorganic chemistry; there is an abundance of new small text-books, of which Erdmann's is the largest and most thorough, but no book to which the student can turn for reference excepting Dammer's "Handbuch," which is simply a reference dictionary and not a treatise of chemistry. Hence the present volume is especially welcome, and it is to be hoped that the one on the metals will appear soon.

Roscoe's manual has a definite place among the other large text-books. While it is not as exhaustive in treatment as Graham-Otto, it mentions every well-authenticated inorganic compound, and gives the more important references to literature. All new technical methods in use occupy sufficient space, and chemical theory, old and new, finds place as well; but the book is distinctly a descriptive rather than a theoretical treatise. Above all it is not too large to study with profit, while it is comprehensive enough to serve as a reference book in most cases.

The new edition is quite up-to-date, as a few examples will show. It includes Baeyer and Villiger's work on hydrogen peroxide and the persulphuric acids; the work of Bone, Lewes and Smithells on flame and the combustion of hydrocarbons; of Dixon on the phenomena of explosion; of Ramsay, Travers and Soddy on the rare gaseous elements in the air and on helium. It gives a full description, with drawings, of the improved processes for making coal gas, with due attention to oil gas, wood gas, water gas, acetylene and the different fuel gases; it describes the various contact processes for the manufacture of sulphuric acid; the electrolytic methods of making chlorine and hydrochloric acid; the manufacture of nitric acid from Chili saltpeter, from ammonia by Ostwald's process, from the air by Bradley and Lovejoy's process.

To praise further "Roscoe and Schorlemmer" is superfluous, as it has established its place in the esteem of chemists. It is enough to say that Sir Henry Roscoe and his coworkers, Dr. Coleman and Dr. Harden, have performed the task of revision with great ability. It is scarcely necessary to add that the publishers have printed and illustrated the book faultlessly.

E. R.